THERMIONIC PHENOMENA

BY

EUGENE BLOCH

Maître de Conférences à la Faculté des Sciences, Paris

TRANSLATED BY

J. R. CLARKE

M.Sc., F.Inst.P.

THIS book can be considered either as being complete in itself, in that it gives a clear and up-to-date outline of our knowledge concerning the emissions from heated bodies, or as an introduction to further study, for there are copious references to original papers. The need for such a book has been felt for some time, and the author has increased its value by a chapter giving an account of some of the applications of thermionic phenomena.

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Dear David,

Thank you very much for the chance to work at the Solid State Theory Group at Imperial College!

With respect to this book by E. Bloch I can only quote Vergil:

"FORSAN ET HAEC OLIM MEMINISSE IUVABIT."

Best wishes,

Albrecht Rau

London, July 1989

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WITH 24 DIAGRAMS

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INTRODUCTION

THE term 'thermionic phenomena' is used to denote the phenomena of electrical conductivity exhibited in the neighbourhood of substances which are raised to a sufficiently high temperature. These phenomena were discovered as early as the eighteenth century but were not investigated in any detail till the middle of the nineteenth. In spite of some interesting investigations, the results remained very incomplete till about 1895, at which time the theory of gaseous ions was developed. This theory having furnished, under the impetus of J. J. Thomson and his students, the directing thread which was lacking in the experimental researches, progress at once became very rapid. During the last twenty-five years our knowledge, both theoretical and practical, of thermionic phenomena has developed without interruption, and industrial applications have followed laboratory researches. Among the most important of these the following may be mentioned: the improvement of electric arcs, the intense and regular production of X-rays, the rectification of alternating currents, and above all the three electrode valves which have recently revolutionized wireless telegraphy and telephony and which at the same time have provided us with a valuable means of investigation and measurement in the most varied domains of electricity.

Thus the subject which we are going to discuss has become very extensive, which does not decrease its difficulty. In fact, we have to deal with a *surface* phenomenon, and it is known from the example of capillarity and from certain optical properties of surfaces how sensitive such phenomena are to the least trace of impurities. The one we are going to study possesses this characteristic to a degree

perhaps even greater than all the others, and this remark enables us to understand some of the difficulties and even contradictions which have been met with in the course of researches carried out to elucidate it. In spite of the accumulation of experiments it is only in the last few years, following progress in vacuum technique and in the manufacture of incandescent filaments, that physicists have been able to arrive at a certain number of simple but firmly established facts in this branch of science. The numerical constants are still not accurate, and the details of the results will have to be reviewed very closely. The confusion apparent in certain parts of this account is a consequence of this situation ; we are not dealing with a question which has been completely cleared up, and which can be presented in a logical and connected manner. But this cause of obscurity is also a cause of interest, and experimental physicists can still find in this branch of science numerous problems worthy of their attention and deserving of more complete exploration.

This short introduction will be concluded by giving some bibliographical information. Mention must first be made of the remarkable book by O. W. Richardson, *The Emission of Electricity from Hot Bodies*,* the latest edition of which (1921) gives the most recent and the most complete information available. I have relied chiefly on this work, which is very thoroughly documented and in which the majority of original papers are mentioned and utilized. I have also been able to make use of certain recent publications, especially American,† and references on the most important points will be found in the footnotes.

* In future, for brevity, this book will be referred to as '*Emission*.'

† A recent lawsuit between the General Electric Company, represented by Irving Langmuir, and the Western Electric Company, represented by Arnold, has been the cause of the publication of detailed depositions by the two parties. I have been able to make use of that of Langmuir (*Langmuir's Record*, 1919), which contains a large number of results, many of them new.

THERMIONIC PHENOMENA

CHAPTER I

HISTORICAL

BEFORE commencing the account of the subject as it is at the present time some historical information will be given.*

As early as the eighteenth century several investigators announced the electrical conductivity of the air in the neighbourhood of heated solids, but the first work wholly on this subject seems to be that of E. Becquerel,† published in 1853. This physicist established, among other things, that a potential difference of a few volts was sufficient to cause the passage of a current measurable by a galvanometer, through air heated between platinum electrodes to a temperature corresponding to red heat. In 1873 Guthrie‡ announced that an iron ball heated till it was a dull red lost a positive charge much more easily than a negative charge. This difference has proved to be only the first example of numerous similar facts which have since been discovered in many domains. In 1881 Blondlot,§ repeating Becquerel's experiments, was able to pass through a heated

* In this connexion see also J. J. Thomson's well-known book *The Conduction of Electricity through Gases*, and Richardson's book mentioned in the Preface. Several of the older fundamental memoirs have been collected in the two volumes published by the Société Française de Physique, edited by MM. Abraham and Langevin, and entitled *Ions, Electrons, et Corpuscles*.

† E. Becquerel, *Ann. de Chimie et de Phys.*, 1853, 39, 355.

‡ Guthrie, *Phil. Mag.*, 1873, 46, 257.

§ Blondlot, *Comptes Rendus*, 1881, 92, 870; 1887, 104, 283.

gas currents which could be measured by an electrometer, with potential differences of only a few thousandths of a volt. At the same time he established that the currents obtained did not satisfy Ohm's law.

A long and interesting series of experiments was carried out between 1882 and 1889 by Elster and Geitel.* These authors heated a metal wire in the neighbourhood of a cold electrode by the passage of an electric current. The heating was carried out in a gas the pressure of which could be varied, and the filament charged positively or negatively ; an electrometer connected to the cold electrode allowed the rate of transfer of the charge through the gas to be followed. It was established in this way that at relatively low temperatures in most cases the current passed more readily when the wire was positively charged than when it was negative. The transfer of negative charges became as easy as that of positive charges at moderately high temperatures, and finally, at the highest temperatures employed, negative currents greatly predominated. These results were confirmed some years afterwards by Branly,† who investigated the rate at which a cold body lost its charge when placed in the neighbourhood of a hot wire.

At about the same time Edison‡ reported an observation which he had made with incandescent carbon filament lamps, and which was the first experience of thermionic emission in high vacua. He had placed in the lamp-bulb an auxiliary electrode situated between the two legs of the filament and equidistant from each. Then, feeding the lamp with a direct current supply, he connected a galvanometer between the auxiliary electrode and one or other of the ends of the filament. By so doing he obtained currents which were very unequal, by far the stronger current

* Elster and Geitel, *Ann. der Phys.*, 1882, 16, 193 ; 1883, 19, 588 ; 1884, 22, 123 ; 1885, 26, 1 ; 1887, 31, 109 ; *Wiener Ber.*, 1889, 97, 1175.

† Branly, *Comptes Rendus*, 1892, 94, 1551.

‡ *Ions, Electrons, et Corpuscles*, p. 183.

being yielded when the galvanometer was connected to the negative end of the filament. This peculiar phenomenon, known as the *Edison effect*, could not be interpreted till many years afterwards. This interpretation was partly the work of Preece * and partly that of Fleming.† The latter remarked that the Edison effect could be used for the rectification of an alternating current, and constructed the *Fleming valve*, the forerunner of modern thermionic rectifiers. Even at that date Fleming conceived the idea of applying the phenomenon to the detection of Hertzian waves, the utilization of which in wireless telegraphy had just commenced.

The researches which have been mentioned remained the work of a few isolated investigators, and the bond which united them did not appear clearly till some years later, when the nowadays classical theory of ions in gases was being developed, in 1895, under the powerful impetus of J. J. Thomson and his students. Thanks to this theory experimental progress, which hitherto had been irregular, was able to become rapid.

According to the theory, all the ordinary cases of gaseous conductivity are due to the same mechanism, namely, the transport of charges by positively and negatively charged ions, each kind being quite distinct from the other, moving with its own velocity and possessing a characteristic charge and mass. From this point of view it became necessary to show that the electrical conductivity in the neighbourhood of heated bodies was also due to ions, and to examine their nature.

The first problem was settled by the experiments of MacClelland,‡ who to a certain extent inaugurated the modern period in the subject we are studying. He caused a current of air to pass over a red-hot platinum wire and showed that this air became conducting; he proved the

* Preece, *Proc. Roy. Soc.*, 1885, 38, 219.
† Fleming, *ibid*, 1890, 47, 118; *Phil. Mag.*, 1896, 42, 52.
‡ MacClelland, *Phil. Mag.*, 1899, 46, 29.

existence of ionization by constructing the saturation curve, and by showing that the current could not exceed a certain limiting value. He also succeeded in measuring the mobility of the ions formed, and rediscovered, in a more quantitative form, the dissymmetry between the charges of opposite signs which had been observed previously by Elster and Geitel.

In order to elucidate the nature of the ions produced, J. J. Thomson* carried out almost at the same time a very celebrated experiment, the 'cycloid' experiment, the historical importance of which is such that the principal thereof will be rapidly reviewed. Let us consider two parallel metallic plates between which a uniform field can be established in a vacuum. In the immediate neighbourhood of one of these plates, A, and parallel to it, is stretched a carbon filament, capable of emitting negative charges when it is raised to white heat. These charges will be collected by the other plate, B, if its potential sufficiently exceeds that of A. The current thus produced is measured by means of an electrometer. If a magnetic field parallel to the filament is now superposed on the electric field, the trajectories of the negative corpuscles will be modified and will tend to assume the form of cycloids. So long as the magnetic field is not too intense the curvature of the trajectories will not prevent the negative corpuscles from arriving at the plate B, and the current measured by the electrometer will not change. But if the magnetic field be progressively increased a time arrives when the summit of the cycloid described by the negative ion falls short of the plate B. The ion then returns towards the plate A, and the current received by B suffers an abrupt decrease. It is easily seen that if the critical magnetic field at which this abrupt decrease is produced is exactly determined, there can be deduced from it accurate information concerning the mechanical and electrical properties of the negative charges emitted by the incandescent filament.

* J. J. Thomson, *Phil. Mag.*, 1899, 48, 547.

The complete theory of the experiment leads to the relation

$$\frac{e}{m} = \frac{2}{d} \times \frac{X}{H^2},$$

where e and m denote the charge and the mass of the negative ion, X and H the intensities of the electric field and of the critical magnetic field, and d the distance between the two plates. From this equation the ratio e/m can be deduced since the other magnitudes are given by the experiment. The result obtained was $0{\cdot}87 \times 10^7$ electromagnetic units. This is only half that obtained for the cathode electrons or corpuscles, for which the accepted value is $1{\cdot}77 \times 10^7$. The experimental errors possible in the method were such that in spite of this difference J. J. Thomson did not hesitate, even at that time, to presume the identity of the negative particles emitted in a vacuum by incandescent filaments with the cathode corpuscles which also exist in vacuum tubes. This view has been confirmed extensively by later experiments. As early as 1904 Wehnelt,* using as a source a heated lime-covered filament, and suitably modifying Thomson's method, obtained the value $1{\cdot}4 \times 10^7$. More recently still, as we shall see, the careful study of thermionic phenomena has allowed much more accurate figures to be obtained, and the quantitative agreement of these with the classical value is altogether satisfactory.

Thus, at the present time, there is no reason to doubt that the negative corpuscles emitted at high temperatures by hot bodies in a vacuum are identical with negative electrons. At lower temperatures there may be also an emission of positive ions, and these, as we shall see, have atomic dimensions.

* Wehnelt, *Ann. der Phys.*, 1904, 14, 425.

CHAPTER II

EXPERIMENTAL ARRANGEMENTS

THE type of apparatus which is always used in the study of thermionic phenomena is shown in Fig. 1. In this figure the incandescent conductor is represented by a wire AB which can be heated to redness by the passage of an electric current. The connexions which serve to lead the heating current in and out are welded to the filament and sealed through the exterior glass bulb, and must have a resistance negligible compared with that of the filament. A cold electrode, shown in the figure as a coaxial cylinder, is placed near to the filament. The bulb can be evacuated or a gas of known composition and at a known pressure can be introduced through a side tube sealed on to the bulb.

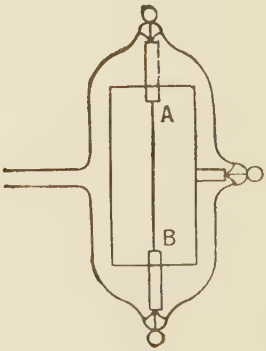

FIG. 1

1. The measurement of the temperature of the heated electrode. The first thing necessary is to raise the filament to a temperature which is known and which can be

accurately adjusted. The constancy of this temperature must be maintained with particular care; we shall see indeed that thermionic phenomena vary extremely rapidly with the temperature, and this is not one of the least of the difficulties encountered in these experiments. In general, it will be advantageous to have the filament made of a material as refractory as possible, in order to increase the utilizable temperature interval, and also to facilitate the cleaning of the filament (see later). In the relatively early experiments the metal most frequently used was platinum, which melts at 1,775° C, and which, as it is not readily attacked, can be subjected to cleaning by the most active chemical reagents. Carbon, which is more readily attacked but much more refractory, was also used in numerous investigations in the early stages.

For some years, however, preference has been given to the study of the most refractory metals such as iridium (melting point, 2,300° C.), molybdenum (melting point, 2,535° C.), tantalum (melting point, 2,780° C.), and especially tungsten (melting point, 3,270° C.). The exact determination of the temperature of the filament is a rather difficult problem. The most usual method consists in using the filament itself as a thermometer and deducing the temperature from its resistance. A preliminary calibration is carried out with a filament identical with that to be used in the experiment, and a Wheatstone's bridge method of measuring the resistance gives all the accuracy desirable. This method would be entirely satisfactory if the temperature of the filament were uniform. Unfortunately, the relatively bulky connexions which are used to lead the heating current in and out of the tube cool the filament near its ends, so that the method only gives a mean temperature, which may differ appreciably from the temperature at the hottest point. The only remedy for this difficulty consists in using a filament sufficiently long for the disturbing effect of the ends to be approximately negligible.

It has also been suggested that the local temperature at various points along the wire might be measured by means of a thermocouple of as small a mass as possible. This method can only give satisfaction when the filaments are so large that the local cooling produced by the presence of the couple need not be taken into account.

Finally, good results appear to have been obtained in recent years by Langmuir and his collaborators employing an optical method. A preliminary investigation has resulted in the discovery of the empirical law connecting the variation of the brightness of a heated tungsten wire with the temperature. Conversely, this empirical law allows the calculation of the temperature of the filament at any point from the simple observation of its intrinsic brightness.

2. The attainment and the measurement of the pressure of the gas. The second technical problem which presents itself in the study of thermionic phenomena is the attainment of a known gaseous pressure and the measurement of this pressure. In particular, it is essential to be able to evacuate the experimental tube as completely as possible in order to avoid the disturbances which may arise from the presence of residual gases. The importance of these effects is only clearly apparent in the most recent researches, and their elimination has only been achieved by making use of all the advances which have been made in vacuum technique. At the present time it is relatively easy to obtain high vacua, thanks to the improved quick-acting pumps, such as Gaede's molecular pump and Langmuir's mercury vapour pump. If the tubes connecting these instruments with the apparatus to be evacuated are sufficiently large, vacua much below a micron of mercury are rapidly attained.

But it is not sufficient merely to create the vacuum ; it must be maintained throughout the experiment, even when the filament is made red hot and when the apparatus

itself assumes a fairly high temperature. In order to do this it is necessary in the first place to interpose a U-tube immersed in liquid air between the pump and the tube to be evacuated ; in this way it is possible to condense the mercury vapour and the water vapour, which might otherwise penetrate into the tube. On the other hand, the filament must be raised to incandescence gradually while the pump is working, in order to get rid of the occluded gases. The glass tube itself must be raised to a temperature of at least 300° C. for about one hour, in order to extract from it all the gases dissolved or occluded, especially water vapour. In certain cases it is even necessary to raise the temperature of the tube still further. To avoid the risk of deformation by its softening under atmospheric pressure the procedure adopted by Langmuir and Richardson can be followed. These investigators heat it in a special furnace which can itself be evacuated, and a temperature of at least 350° C. is thus attained without danger.

Finally, it is essential to degasify the cylinder which is to serve as the anode, the temperature of which will remain relatively low during the measurements. To do this, the filament is made red hot and used as the cathode in an electric discharge, the cylinder being the anode and the tension applied being of the order of 1,000 volts. The cathodic corpuscles emitted by the filament and accelerated by the electric field give up their kinetic energy to the anode cylinder and rapidly raise it to red heat. A liberation of gas results which causes a bluer glow to appear in the tube, this being a sign of ionization by collision and consequently of the presence of gas. The corpuscular bombardment is temporarily interrupted as necessary to give the pump time to evacuate the gas liberated and to avoid the formation of an arc ; by repeating this heating and cooling several times a stage is reached fairly rapidly when a good vacuum can be maintained in the tube while both the cathode and the anode are red

hot. If care has been taken to raise the temperatures of the two electrodes above the maximum values which they will attain in the course of the thermionic experiments the vacuum obtained will be perfectly stable. It may be remarked in passing that the anode must be made of a metal which is also sufficiently refractory to withstand high temperatures. Nickel, platinum, molybdenum, and even tungsten are widely used for this purpose.

Even when the vacuum has been obtained it is still necessary to measure it. In addition, it is desirable in some cases to introduce into the tube a trace of a known gas, the pressure of which must also be determined. Twenty years ago the vacua ordinarily realizable rarely exceeded a thousandth or a ten-thousandth of a millimetre of mercury. They were measured with a McLeod gauge, which gives very nearly accurate results up to this limit, if the pressure of the mercury vapour be neglected. At the present time much higher vacua are reached, the pressures being of the order of 10^{-5} to 10^{-7} microns of mercury, and thus quite a new technique has had to be developed in order to measure them. Some of the methods employed are based on the molecular properties of very rarefied gases, such as the viscosity and thermal conductivity. Other methods which themselves make use of thermionic phenomena will be described briefly later.*

3. The measurement of the currents. When the experimental tube has been evacuated and its filament raised to a known high temperature it remains to measure the thermionic currents which can be made to pass through the rarefied gas by a difference of potential applied between the two electrodes. The intensity of these currents varies with the experimental conditions to a very large extent. In some cases the currents are of the order of 10^{-14} or 10^{-12} amperes. They are then measured with an electrometer, which is the only instrument sufficiently

* For details see *La Technique du Vide* by L. Dunoyer.

sensitive to record them. When the currents reach 10^{-9} or 10^{-8} amperes galvanometers can be substituted for electrometers. If the current becomes of the order of 10^{-4} amperes direct reading milliammetres are used. Finally, there are thermionic tubes capable of yielding currents of several amperes; the measuring instrument is then an ordinary ammeter.

The general result which has been obtained in all thermionic measurements can be summarized by the diagram given in Fig. 2. This figure shows the variation of the current with the applied voltage, the measurements being assumed to be made at a constant temperature. It is

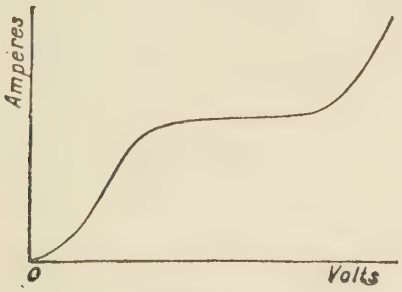

FIG. 2

seen that the current increases at first with the voltage, then reaches a stationary value (the saturation current), until the time when the ionization by collision between the electrons, and the molecules of the residual gas causes the curve to resume its upward trend, thus leading on to the phase of disruptive discharge. The various portions of this curve are very unequally developed according to the conditions. For example, if the vacuum is very high and the filament at a lower potential than that of the cylinder (the case of an electronic current), the second ascending portion of the curve which corresponds to ionization by

collision completely disappears. On the other hand, if the filament is charged positively and the temperature and the vacuum are only moderately high, the region of saturation can never be obtained.

Finally, let it be remembered that at temperatures which are relatively low, the emission consists almost solely of positive ions, at medium temperatures electrons or negative ions begin to be mixed with them, and eventually at high temperatures, especially in a good vacuum, only the negative corpuscles are present.

We shall commence the detailed account of the experimental results by the study of the most important case, that of the *pure electron emission*, i.e. of the emission of negative corpuscles which carry by themselves the whole of the current in the best vacua and at the highest temperatures. In this way we shall acquire the information necessary for the study of the much more complex phenomena which present themselves when a gas is present or when positive ions come into consideration.

CHAPTER III

THE ELECTRONIC EMISSION IN A VACUUM: THEORETICAL INVESTIGATION

1. The initial theory and Richardson's law. The first theory of pure electronic emission in high vacua was given by O. W. Richardson in 1901,* and was very soon verified experimentally. This theory was intimately connected with the kinetic theory of metals which was accepted at that time. A brief account of it will be given, attention being concentrated particularly on the guiding ideas.

In the kinetic theory of metals† as it has been built up by Riecke, Drude, J. J. Thomson, and H. A. Lorentz, metallic conductors are assumed to contain large numbers of free electrons, the motions of which due to thermal agitation are identical with these of an ordinary gas at the same temperature. The motions of these free electrons are continually being affected by their collisions with the atoms of the metal, which can be regarded as being very nearly immobile. Nevertheless, under the influence of an electric field or of a temperature gradient the electrons tend to acquire a collective motion in the same direction as the fall of potential or temperature. On this theory such is the origin of the electric or thermal conductivity of metals as well as of thermionic phenomena.

That this electronic gas within the metal does not escape to the exterior is because it is prevented from so doing by the existence of a transition layer at the surface of the metal, and the electrons can only pass through this

* Richardson, *Proc. Camb. Phil., Soc.* 1901, 11, 286.

† Concerning this theory see, for example, E. Bloch, *La Théorie cinétique des Métaux*, in the book *Conférences sur la Constitution de la Matière*, published by the Société Française de Physique in 1913.

layer by the expenditure of a certain amount of energy. To be more definite, it may be supposed that there exists at the surface a Helmholtz double layer, the positive face of which is turned towards the metal and the negative face towards the exterior. If V denotes the difference of potential between the metal and the vacuum, and e the charge on an electron, the latter can only escape from the metal if its kinetic energy due to its velocity in a direction normal to the surface is at least equal to the value $\varphi = e\mathrm{V}$.* The normal component of its velocity must therefore attain a value at least equal to u_o, given by the equation

$$\tfrac{1}{2}mu_o^2 = e\mathrm{V}. \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Let us suppose the metal to be placed in an insulating evacuated enclosure at a uniform temperature. The electrons which leave the metal will form an external atmosphere of electrons, more rarefied than the internal gas, and the corpuscles which constitute it will gradually reach statistical equilibrium with those of the internal gas owing to the exchange of corpuscles between the two.

When this state is attained the total number of electrons emitted per second per square centimetre of the metal can be calculated without difficulty from the principles of the kinetic theory of gases applied to the internal gas, and hence the electronic current corresponding to this emission can be obtained. In fact, if n is the number of free electrons per cubic centimetre in the interior of the metal, and dn the number which have a velocity component

* The case in which the work of extraction ϕ of an electron is larger than the purely electrical work $e\mathrm{V}$ cannot be excluded *a priori*. In the general case the mechanical energy (the sum of the kinetic and potential energies calculated without reference to the electric charge) will not be the same for an internal electron as for an external electron, so that ϕ will differ from $e\mathrm{V}$. For the sake of simplicity this difference is here neglected.

normal to the surface between u and $u + du$, then the kinetic theory* shows that

$$dn = n\sqrt{\frac{hm}{\pi}}\, e^{-hmu^2}\, du, \quad \ldots\ldots\ldots\ldots (2)$$

where h is a constant related to the absolute temperature by the equation

$$h = \frac{1}{2k\mathrm{T}}, \quad \ldots\ldots\ldots\ldots\ldots (3)$$

and k is the perfect gas constant referred to a single molecule.

It follows from equation (1) that only those electrons can leave the metal which have velocity components normal to the surface satisfying the condition $u \geqslant u_0$ or $u \geqslant \sqrt{\frac{2\varphi}{m}}$. The intensity of the electron current emitted per square centimetre of surface of the metal will be

$$\text{therefore} \quad i = \int_{u_0}^{\infty} ue\, dn = ne\sqrt{\frac{hm}{\pi}} \int_{\sqrt{\frac{2\varphi}{m}}}^{\infty} e^{-hmu^2} u\, du$$

or

$$i = a\,\mathrm{T}^{\frac{1}{2}} e^{-\frac{b}{\mathrm{T}}} \quad \ldots\ldots\ldots\ldots (4)$$

where

$$a = ne\sqrt{\frac{k}{2\pi m}} \quad \ldots\ldots\ldots\ldots\ldots (5)$$

and

$$b = \frac{\varphi}{k} = \frac{e\mathrm{V}}{k}. \quad \ldots\ldots\ldots\ldots\ldots (6)$$

If it could be assumed that n and V were independent

* See, for example, E. Bloch, *The Kinetic Theory of Gases*, Methuen & Co., Ltd.

of the temperature, the same would apply to the parameters a and b, and the formula (4) would then give the law of the variation of the saturation current emitted by a square centimetre of surface as a function of the absolute temperature. This equation is called ' Richardson's equation ' or ' *Richardson's law.*' It plays a fundamental part in the study of thermionic phenomena on account of the very exact representation which it gives of all the experimental facts (see Chapter IV). Under all conditions it is possible to choose the numerical constants a and b so as to cover the results of measurements.

Reference to the equations (5) and (6) shows that a knowledge of a enables n to be calculated, and that if b is known V can be ascertained. The first calculation is not of any particular interest ; in fact, we shall see later that there are important doubts as to the exact significance of the constant a. On the other hand, the calculation of V based on the knowledge of b is of considerable importance. It yields a method of determining, indirectly it is true, the contact difference of potential between a metal and the surrounding medium.

2. The thermodynamical theory. An important development of Richardson's first theory was made by H. A. Wilson,* who showed shortly after the publication of Richardson's work that the equation could also be obtained by arguments based on thermodynamical principles, and hence much more rigid than the original argument. The theory of H. A. Wilson has been completed since then by J. J. Thomson† and Richardson.‡

In the thermodynamical theory we retain the conception

* H. A. Wilson, *Phil. Trans.*, 1901, 197, 429.

† J. J. Thomson, *Phil. Trans.*, 1903, 201, 502.

‡ Richardson, *Jahrbuch der Rad. und Electronik*, 1904, 1, 302 ; *Phil. Mag.*, 1912, 23, 263 and 602 ; 1912, 24, 737 ; 1914, 28, 633 ; *The electron theory of matter*, 1914, p. 448 ; *Emission*, 1921, p. 32.

See also, H. A. Wilson, *Phil. Trans.*, 1903, 202, 258 ; *Phil Mag.*, 1912, 24, 196 ; Debye, *Ann. der Phys.*, 1910, 33, 469.

that the electrons exterior to the metal and in thermal equilibrium with it constitute an actual gas which has all the properties of a perfect gas, and the molecules of which, in particular, conform to Maxwell's velocity distribution law. This hypothesis is rendered very probable *a priori* by the extreme minuteness of the particles concerned (molecules of negligible dimensions) and by the rarefaction of the gas at moderate temperatures. It is true that the electrons which constitute the gas exercise on one another repulsive electric forces, varying inversely as the square of the distance between them, these forces giving rise to a sort of negative pressure analogous to that of van der Waals' equation, but the rarefaction of the gas at moderate temperatures renders these actions practically negligible. Thus the external electrons seem to constitute a gas which agrees better than many others with the definition of a perfect gas. Moreover, we shall see later (Chapter V) that experiment has fully confirmed this view, which can consequently be used as a valid basis for thermodynamical arguments. In particular, if p denotes the pressure of the external electronic gas, v its volume, and T the absolute temperature of the system, the classical equation

$$pv = \mathrm{RT} = \mathrm{N}k\mathrm{T} \quad \ldots\ldots\ldots\ldots\ldots (7)$$

holds, where N is Avogadro's number, and R and k are respectively the constants of a perfect gas with respect to a gramme molecule and to a single molecule, assuming that the volume is sufficiently great for the total mass to be that of a gramme molecule. On the other hand, if n is the number of electrons per cubic centimetre of the gas, the kinetic theory gives the relation

$$p = \frac{n}{2h} = k\mathrm{T}n. \quad \ldots\ldots\ldots\ldots\ldots (8)$$

Finally, the number of electrons which strike one square centimetre of the surface of the metal per second is

$$n' = \frac{n}{2\sqrt{\pi hm}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The application of the kinetic theory of gases to the system consisting of the electrons *within* the metal, on the contrary, appears to be much less legitimate at the present time than it was at the time when Richardson first advanced his theory. In fact, important experimental discoveries have thrown some discredit on the old kinetic theory of metals. In particular, the considerable decrease in the specific heat of metals at low temperatures, and the appearance of the state of ' supraconductivity ' under the same circumstances appear to be difficult to reconcile with the old kinetic conceptions. It remains beyond doubt that the explanation of the electrical and thermal conductivity of metals must continue to be sought in the transfer of electrons within the metal, but these electrons may only be free for a small part of the time, so that it is not at all legitimate to apply to them laws founded on the equipartition of energy and on classical statistical mechanics. There is no doubt that here again the quantum theory must be called in to explain the question completely. However this may be, the only hypothesis which it appears legitimate to apply to the system of electrons within the metal is its similarity to a kind of condensed fluid which enters into equilibrium with the external gas just as does a liquid with its vapour, but the exact kinetic properties of which remain unknown.

The equilibrium condition is nevertheless governed by the laws of thermodynamics, and Clapeyron's formula can be applied to it. We will write this in the form

$$\mathrm{L} = v\mathrm{T}\frac{dp}{d\mathrm{T}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

where L is the latent heat of vaporization of a gramme molecule of electrons, the volume of the internal electronic fluid being supposed negligible with respect to that of the external gas. The work necessary to extract an electron from the metal has already been denoted by φ. The total heat of evaporation will be obtained by adding to this work the external work done by the isothermal expansion of the gas, and this leads to the classical relation

$$L = N\varphi + pv = N(\varphi + kT).$$

The equation (10) then becomes

$$k\frac{dp}{p} = \frac{\varphi + kT}{T^2}\,dT,$$

whence

$$p = aT\,e^{\int \frac{\varphi}{kT^2}\,dT} \quad \ldots\ldots\ldots\ldots (11)$$

But, if thermodynamical equilibrium be attained, the number of electrons which strike one square centimetre of the surface of the heated metal per second is the same as the number of electrons which leave the surface during the same time, provided that it is assumed that the number of electrons reflected by the metal is negligible. It follows from equation (9) that the electrons emitted will carry a current

$$i = \frac{ne}{2\sqrt{\pi hm}},$$

or, again, using equations (3), (8), and (11)

$$i = aT^{\frac{1}{2}}e^{\int \frac{\varphi}{kT^2}dT}, \quad \ldots\ldots\ldots\ldots (12)$$

where a is a constant independent of the temperature.

In order to proceed further it is necessary to know the relation between φ and T. If it be assumed, in the first place, that φ is independent of T, the formula (12) takes the form

$$i = aT^{\frac{1}{2}}e^{-\frac{\varphi}{kT}},$$

which is identical with (4). That is to say, Richardson's law again appears under its old form. But, as Richardson himself has shown,* the hypothesis of the constancy of φ is very improbable, and even difficult to reconcile with the existence of thermoelectric phenomena. To obtain the connexion between the work of extraction of an electron and the temperature Richardson has used thermodynamical arguments which involve both thermionic and thermoelectric phenomena. We shall not enter into the details of these arguments here; they are to be found either in one of Richardson's books mentioned in the footnote on page 16 or in the original papers; we shall merely state the result which has been obtained. Richardson shows that if it is possible to neglect the specific heat of electricity, the magnitude of which governs the Thomson effect, we can write

$$\varphi = \varphi_0 + \frac{3}{2}kT.$$

Thus the work of extraction of an electron would be approximately a linear function of the absolute temperature.

If this is the case, the general equation (12) takes the form

$$i = aT^{\frac{1}{2}}e^{-\frac{\varphi_0}{kT}}, \quad \ldots\ldots\ldots\ldots\ldots (13)$$

where a and φ_0 denote magnitudes which are independent of the temperature.

* Richardson, *Emission*, p. 32.

To sum up, it is seen that the preceding theories give a formula of the type

$$i = aT^n e^{-\frac{b}{T}}, \quad \ldots\ldots\ldots\ldots\ldots (14)$$

for the total current (saturation current) emitted by one square centimetre of surface of the metal. In this formula a and b are constants independent of the temperature, and n is a number of the order of unity. Further, the constant b is connected in a simple manner with the contact difference of potential between the metal and the external medium (Equation 6).

3. Other theories. Of the other theories of electronic emission which have been advanced one or two will be mentioned, these being of interest for various reasons.

In the first place, Richardson* has attempted to complete the thermodynamical arguments, which have just been developed, by *quantum* considerations. These considerations are somewhat complicated and do not appear to be entirely free from objection. Also it will be sufficient for our purposes to say that the formula (13) is again obtained, with the additional characteristic that the constant a should be the same for all substances. It will probably be necessary to revise this theory before all its conclusions can be accepted.

Again, it is possible to conceive a *photoelectric* theory † of the phenomenon. The incandescent metal emits visible and ultraviolet radiations and the electronic emission observed at high temperatures can be considered to be due to a photoelectric effect of these radiations on the metal itself. It appears, however, that the quantitative data which we possess on the photoelectric effect allow this cause of emission to be eliminated in the majority

* Richardson, *Phil. Mag.*, 1914, 28, 633; *Emission*, p. 37.
† Ibid., *Emission*, p. 110.

of cases as being of an order of magnitude which is insufficient.

Finally—and this is a point of view worthy of holding our attention—certain physicists have proposed a *chemical* theory of the phenomena. In fact, in this branch of science, as in so many others, there exist two opposing points of view, which may be called the *intrinsic* and the *chemical* standpoints. To the partisans of the former thermionic emission is a property characteristic of incandescent conductors, even when these are rigorously pure and heated in the most perfect vacuum. To the others, on the contrary, the phenomena observed are due to chemical reactions between the heated metal and the traces of residual gas which arise from the vacuum being insufficient or from the continual liberation of gas by the metal itself. This latter point of view has been energetically maintained by many physicists of the German school, and a large number of experimental facts, the chief of which will be examined, appear at first sight to confirm it.* At the present time, however, though the preponderating role of chemical actions in a certain number of cases (alkali metals, according to the experiments of Haber and Just, and so on) cannot be disputed, it seems more and more evident that the intrinsic theory is much the most probable in the truly typical cases; we shall see the important arguments which nowadays can be advanced in its favour.

For the time being it will be sufficient to observe that the study of the law of the variation of the thermionic emission as a function of the temperature cannot be used to decide between the two theories. In fact, it can be shown that the chemical theory leads to the derivation of a relation expressing the saturation current as a function of the temperature which contains, as does Richardson's law, an exponential of the form $e^{-\frac{b}{T}}$. As this exponential term altogether preponderates in Richardson's formula,

* Richardson, *Emission*, p. 147 et seq.

its presence is no more in favour of the chemical theory than of the intrinsic theory.

4. Relations with the contact potential difference. This chapter which has been devoted to theoretical considerations will be concluded with a few remarks concerning the relations which exist between the phenomena of thermionic emission in a vacuum and contact differences of potential.

It is known that if two different metals (zinc and copper, for example) are placed facing one another in a vacuum and connected to each other by a conducting wire, there exists between two points A and B near to the surfaces of these two metals a potential difference, which is called ' the contact potential difference '. For a century these potential differences have been the object of innumerable measurements and of intense discussions. In fact, the chemical theory and the intrinsic theory are again found to exist. To the upholders of the former this contact difference of potential must be attributed to the chemical actions between the metal and traces of surrounding gas, and in particular of water vapour. If this standpoint is correct the differences should disappear entirely if pure metallic surfaces were obtained in a perfect vacuum. This is what seems actually to occur in some of the most recent experiments on this subject.*

On the other hand, if the intrinsic point of view be adopted the difference of potential should exist even in an absolute vacuum, and is essentially a property characteristic of the two metals under consideration.

We cannot pretend to settle in a few words so old a question, but it is important from the point of view which interests us to show the very intimate connexion which exists between the contact potential differences and the thermionic emissions. If the latter are intrinsic properties of all metals, and if the intensity of the electronic emission

* On this subject the papers mentioned in Richardson, *Emission*, pp. 45 and 46, may be consulted. See also Millikan, *Phys. Rev.*, 1921, 18, 236.

is not the same for all metals at all temperatures, it necessarily results that the contact potential differences also have an intrinsic existence. On the other hand, if the potential differences have not an intrinsic existence it must be concluded that this is also true of the thermionic emissions, or at least that these emissions should be the same for all metals at the same temperature.

Indeed, let us consider two metallic plates made of different metals (for example, tungsten and molybdenum), connected by a conducting wire and raised to a uniform and sufficiently high temperature in a perfect vacuum. Both the metals will emit electrons, and if the characteristic emission of the first exceeds that of the second an equilibrium state will be set up in which the first will be charged positively with respect to the second. A point A near the surface of the first will therefore be at a higher potential than a point B near the surface of the second: there will be a contact difference of potential. Let V be the value of this difference and n_1 and n_2 the numbers of electrons per cubic centimetre of the medium at A and B respectively when the stationary state is attained. The work necessary to carry an electron from A to B is eV, and the laws of statistical mechanics which are applicable, as we have seen above, to the electronic gas, enable the work eV to be calculated if the equilibrium electronic densities n_1 and n_2 are known. Boltzmann's general equipartition theorem, in fact, gives the relation

$$\frac{n_1}{n_2} = e^{-\frac{e\mathrm{V}}{k\mathrm{T}}}.$$

If it be assumed, in accordance with the theories developed at the beginning of this paragraph, that the saturation currents i_1 and i_2 which can be obtained from the two metals are proportional to n_1 and n_2, we can also write

$$\frac{i_1}{i_2} = e^{-\frac{e\mathrm{V}}{k\mathrm{T}}}.$$

Thus, if the two metals have different thermionic emissions, which implies that these emissions are intrinsic properties of the two metals, the difference of potential V is necessarily different from zero. Conversely, if the thermionic emissions are identical, or if they are nil (the hypothesis assumed in the chemical theory), the difference of potential disappears.

We shall see later to what extent the experimental results confirm or invalidate the two different points of view.

It would be very interesting to continue to develop considerations of this type and to apply them in particular to the study of the intimate relations which exist between thermionic phenomena and thermoelectric phenomena. But, in spite of the very noteworthy efforts which have been made in this direction by several physicists, it does not seem that there is, as yet, a theory which is entirely satisfactory in all its details, and it will be sufficient to give references to books and original papers on this topic.*

* In particular, see Richardson, *The Electron Theory of Matter*, (Cambridge University Press), and the following papers :

Richardson, *Phil. Mag.*, 1912, 23, 263 ; 1912, 23, 594 ; 1912, 24, 737.

Bohr, *Phil. Mag.*, 1912, 23, 984.

Kruger, *Phys. Zeits.*, 1910, 11, 800 ; 1911, 12, 360.

CHAPTER IV

THE ELECTRONIC EMISSION IN A VACUUM: EXPERIMENTAL RESULTS

SINCE Richardson's first experiments,* carried out with a view to verifying the theoretical formulae of the preceding chapter, the experimental material relating to this question has assumed very large proportions. It is out of the question to give here a really complete bibliography of the subject, and for the details reference should be made to Richardson's book, which has been mentioned so frequently. It may be stated, however, that after the first paper by Richardson, which dealt with platinum, carbon, and sodium, the examination of platinum was very soon repeated in detail by H. A. Wilson † and by Richardson himself. Very shortly afterwards Wehnelt's important discovery ‡ of the intense electronic emission from the oxides of the alkaline earths (Wehnelt cathodes) was made. The experiments were continued by Owen § on the filament of the Nernst lamp, by Deininger‖ on platinum, carbon, tantalum, and nickel, pure and covered with lime, by Horton ¶ on platinum covered with calcium and lime, by Martyn** on Wehnelt cathodes in air and in hydrogen, by Jentzsch†† on numerous metallic oxides, by

* Richardson, *Proc. Camb. Phil. Soc.*, 1901, 11, 286; *Phil. Trans.*, 1903, 201, 497; 1906, 207, 1.

† H. A. Wilson, *Phil. Trans.*, 1903, 202, 243; 1908, 208, 247.

‡ Wehnelt, *Sitz. der Phys. med. Soc. Erlangen*, 1903, p. 150; *Ann. der Phys.*, 1904, 14, 425; *Phil. Mag.*, 1905, 10, 88.

§ Owen, *Phil. Mag.*, 1904, 8, 230.

‖ Deininger, *Ann. der Phys.*, 1908, 25, 285.

¶ Horton, *Phil. Trans.*, 1907, 207, 149.

** Martyn, *Phil. Mag.*, 1907, 14, 306.

†† Jentzsch, *Ann. der Phys.*, 1908, 27, 129.

Fredenhagen* on sodium and potassium, and by Pring and Parker † on carbon. In more recent times work has been carried out with more refractory materials, which has enabled still more intense electronic currents to be obtained, and more clearly defined conditions to be specified. If it be remembered that the most important advances in vacuum technique have been made in the same period, it will be understood that this period, which can be called the contemporary period, has been exceedingly rich in important results. Particular mention must be made of the fundamental experiments of Langmuir ‡ on tungsten, tantalum, molybdenum, platinum, thorium, and carbon; those of Richardson § and Smith || on tungsten; those of Schlichter ¶ on platinum and nickel; those of Stoeckle** on molybdenum; those of Dushman †† on titanium and iron; and those of Arnold ‡‡ on Wehnelt cathodes.

1. The verification of Richardson's law. The first general result which has been obtained in all the experiments is as follows: the electronic emission which is inappreciable at ordinary temperatures can be observed at 200° C. with the alkali metals. For the others it is clearly apparent only at very much higher temperatures, which are of the order of 1,000° C. for the more refractory metals. In all cases the increase of the emission with temperature is very rapid and follows an exponential

* Fredenhagen, *Verh. der Deutsch. Phys. Ges.*, 1912, 14, 386.

† Pring and Parker, *Phil. Mag.*, 1912, 23, 192; Pring, *Proc. Roy. Soc.*, 1913, 89, 344.

‡ Langmuir, *Phys. Rev.*, 1913, 2, 450; *Phys. Zeits.*, 1914, 15, 525; *Trans. Amer. Electrochem. Soc.*, 1916, p. 354; *Langmuir's Record on the electron tube*, U.S. Patent Office, 1919.

§ Richardson, *Phil. Mag.*, 1913, 26, 345.

|| Smith, *Phil. Mag.*, 1915, 29, 811.

¶ Schlichter, *Ann. der Phys.*, 1915, 47, 573.

** Stoeckle, *Phys. Rev.*, 1916, 8, 534; See also 1917, 9, 503 (Richardson's comments).

†† Dushman, quoted by Langmuir, *Trans. Amer. Electrochem. Soc.*, 1916, p. 534.

‡‡ Arnold, *Phys. Rev.*, 1920, 16, 73.

law. To illustrate this result some of the curves contained in Richardson's fundamental memoir (*Phil. Trans.*, 1903)

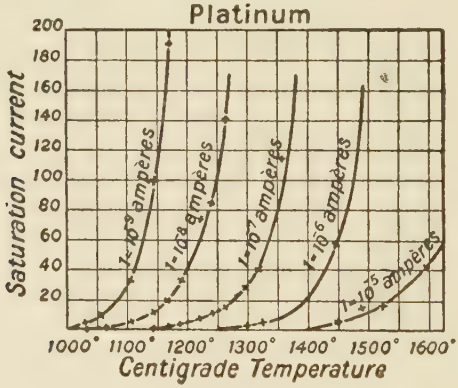

FIG. 3

are reproduced; these curves relate to platinum, carbon, and sodium (Figs. 3, 4, and 5). In order to be able to plot the whole of the results for a particular substance on one

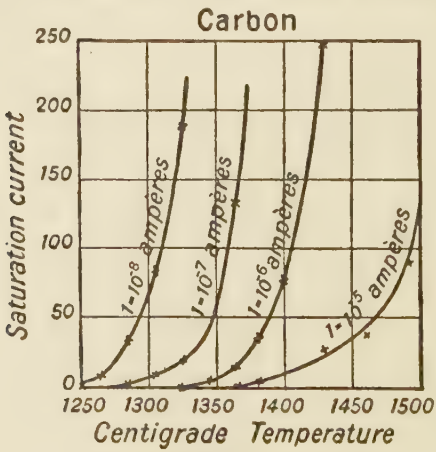

FIG. 4

graph the ordinates have been reduced in the ratio 10 to 1 after a first branch has been drawn for a relatively low temperature before proceeding to the next curve, and so on. It is seen that for platinum the electronic currents changed from 10^{-9} amperes to 4×10^{-4} amperes, when the temperature rose from 1,000° C. to 1,600° C. For carbon, the current increased from 10^{-8} amperes to 10^{-3} amperes between 1,250° and 1,500°. Finally, for sodium the

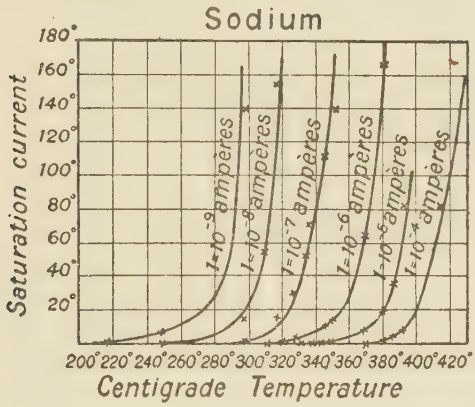

FIG. 5

variation is still more rapid, since the current increases from 10^{-9} amperes to $1{\cdot}4 \times 10^{-2}$ amperes with a temperature change of only 210 to 430 degrees.

The first question which presents itself concerning these curves is to know how far they agree with the theoretical formulae established in the preceding chapter. As has been seen, these formulae are of the type

$$i = a\,T^n\,e^{-\frac{b}{T}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

n being a number of the order of unity; in Richardson's first formula n was equal to $\frac{1}{2}$, in the more recent and more accurate formula, based on thermodynamics, n is equal to 2.

In order to attempt to decide between these formulae a graphical method can be employed. The values of 1/T are plotted as abscissae and of log $i - n$ log T as ordinates, making n successively equal to $\frac{1}{2}$ and 2. Fig. 6 has been obtained in this way using the results obtained by Deininger * with a Wehnelt cathode. It is apparent that the points are situated as rigorously on the straight line for which n is equal to $\frac{1}{2}$ as on that for which n is equal to 2. This also occurs when the currents vary to a much greater degree, as, for example, in the experimental results of

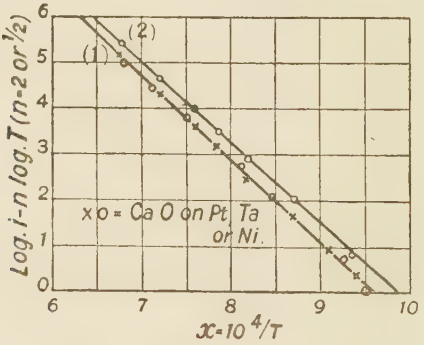

FIG. 6

Smith † on tungsten, where the currents increased in the ratio of 10^{11} to 1.

Thus the general formulae (15) is very exactly verified in all cases, without it being possible to decide the exact value of the index n. The majority of authors use the older formula, putting n equal to $\frac{1}{2}$, and we shall follow their example. The numerical representations so obtained are very exact, but it should be remembered that the numerical value of the constant a cannot be considered as having a very definite theoretical meaning. On the

* *Loc. cit.* † *Loc. cit.*

other hand, the constant b which occurs in the exponential term, the only important one, has an essential significance. The least variation of this constant, moreover, has a great effect on the magnitude of the electronic current.

In conclusion, let us mention the sole exception to the validity of Richardson's formula which has been discovered up to the present. This exception, announced by Richardson and Cooke,* is in the case of osmium: the straight lines of the preceding graph are replaced by a broken line made up of two straight lines inclined to each other at a definite angle. It is probable that two allotropic modifications of osmium exist, each of which has its characteristic emission, there being a transformation point at a certain temperature.

2. Values of the constants. In order to proceed farther it is necessary to determine the values of the constants a and b of Richardson's formula for the various incandescent conductors. The knowledge of these constants is essential to the prediction of the electronic currents which can be obtained from a given conductor raised to a known temperature; it is of very great practical importance.

If the electronic emission can be considered as an intrinsic property of the substances the constants will have perfectly definite numerical values for each substance, and a table of these constants will be sufficient to characterize the substances. On the other hand, if the chemical theory, which attributes the effects observed to the reactions between the conductor and traces of the residual gas, is to be accepted, it is possible to predict a very large variation in the values of the constants obtained for the same metal by different observers, since these constants will be directly dependent on the method adopted for purifying the metal or gas.

The earlier results appeared to support the chemical

* Richardson and Cooke, *Phil. Mag.*, 1911, 21, 408.

theory. In the relatively early researches on platinum and carbon, for example, there are to be found numerical values of the constants which seem to be irreconcilable with each other and hence incompatible with the idea of an intrinsic property. All these results are collected in Richardson's book, and their value is thoroughly discussed. On the contrary, the most recent experiments, carried out with very refractory metals and with all the precautions known to be necessary in vacuum technique, have yielded numerical values which approximate to each other more and more. It may be assumed that for substances such as tungsten the values of the constants are known at the present time with a fair degree of accuracy, and that the very agreement between the results is sufficient to serve as an argument in favour of the intrinsic theory. The table on page 33 gives the numerical values of the constants for the conductors, which appear to have been most accurately examined so far. The most reliable figures are those which relate to tungsten; those for molybdenum and tantalum should be redetermined; those for carbon and platinum are still open to discussion; the others are only given here to indicate the order of magnitude. The table does not contain any data on the emission of compounds (Wehnelt cathodes, etc.); we shall return to this question later. The units are chosen so that the current i in Richardson's formula is given in amperes per square centimetre of emitting surface.

For the very oxidizable metals such as calcium and sodium it is possible that the chemical theory should be accepted. In fact, it is known, from the experiments of Haber and Just, and the complementary experiments of Richardson,* that sodium emits electrons when it is chemically attacked by certain gases such as phosgene ($COCl_2$); and the part played by gases is not entirely excluded in the experiments hitherto made with these

* In this connexion see, for example, Richardson, *Emission*, p. 307 et seq.

Metal	a	b	Authors
Tungsten	$24{\cdot}8 \times 10^6$	52,500	Langmuir, *Phys. Zeits.*, 1914
	$23{\cdot}6 \times 10^6$	52,500	Dushman, *Gen. Electric Rev.*, 1915
Tantalum	$11{\cdot}9 \times 10^6$	50,000	Langmuir, *Phys. Rev.*, 1913
Molybdenum	22×10^6	50,000	Langmuir, *Phys. Rev.*, 1913
Platinum	$3{\cdot}2 \times 10^{12}$	80,000	Langmuir, *Phys. Rev.*, 1913
	$11{\cdot}5 \times 10^6$	51,100	Schlichter, *Ann. der Phys.*, 1915
Carbon	$2{\cdot}38 \times 10^6$	48,700	Langmuir, cited by Richardson
Thorium	2×10^8	39,000	Langmuir, *Trans. Amer. Electrochem. Soc.*, 1916
Titanium	13×10^2	28,000	Dushman, preliminary measurements cited by Langmuir
Iron	24×10^2	37,000	
Nickel	$4{\cdot}84 \times 10^6$	34,000	Schlichter, *Ann. der Phys.*, 1915
Calcium	$1{\cdot}76 \times 10^4$	36,500	Horton, *Phil. Trans.*, 1907
Sodium	$1{\cdot}6 \times 10^{12}$	31,600	Richardson, *Phil. Trans.*, 1903

metals. In any case, it is desirable that this examination should be repeated from this point of view, taking advantage of the facilities which are at present available for eliminating gaseous impurities.

On the contrary, for all the other metals in the list (with the possible exception of platinum) as well as for carbon, it appears that in spite of the inaccuracy in the numerical data, which frequently is still rather great, there are strong reasons for supporting the intrinsic theory of emission. In what follows we shall come across new and fairly numerous arguments in favour of this view.

The knowledge of the constants of electronic emission is important from many points of view. For example, the constants for tungsten are sufficiently well known for the emission from a given filament at any temperature

whatsoever to be calculated *a priori* with reasonable accuracy. Thus a calculation made for a temperature of 3,600 degrees absolute shows that tungsten emits two *amperes* per square centimetre. With the filament surfaces now available the currents may be as great as several tenths of an ampere and may even exceed an ampere. As we shall see, it is this which is the cause of the importance of tungsten and all the other very refractory elements as sources of thermionic currents.

Another interesting consequence which follows from the knowledge of the constant b is the calculation of the contact potential difference between the metal and a vacuum, or, more accurately, of the work of extraction of an electron. This quantity may be deduced from the equation (6), page 15 (see also the note at the foot of page 14).

$$b = \frac{\varphi}{k} = \frac{eV}{k}.$$

If both terms of the fraction are multiplied by Avogadro's constant N, the numerator will contain the factor Ne, the charge carried by one gramme-ion of hydrogen in electrolysis, or 9,650 electromagnetic units. The denominator will become Nk = R, the gas constant referred to a gramme-molecule, or $8{\cdot}32 \times 10^7$ C.G.S. units. Thus the value of the contact potential difference V can be deduced without ambiguity from that of b. The values obtained by using the numbers in the preceding table are mostly of the order of three volts, which is a very reasonable order of magnitude. It certainly would be extremely interesting to check the values so obtained by direct measurements of the contact potential differences. But, in addition to the fact that these measurements would only lead to rather complex combinations of the values of V for various metals, the measurements would have to be made under the same conditions as the thermionic measurements, i.e. at red heat ; to do this would be very difficult. Finally, in the

case of those metals which have been most thoroughly examined, for example, molybdenum and tungsten, the constants b, and hence the potential differences V, differ from each other by a relatively small amount (perhaps this difference may even be nil), and this circumstance will not make the measurement of the contact potential difference any easier. Hence it is not very surprising that these verifications have not been carried out as yet; there is here an interesting subject for research in the future.

3. The thermionic emission from compounds in a vacuum: Wehnelt cathodes. The property of emitting electrons at high temperatures in a vacuum is one possessed by compounds as well as by elements. The first investigation of this subject was made by Wehnelt.* This physicist established, in 1903, that the cathode fall of potential in a vacuum tube is greatly diminished when the cathode is covered with a thin layer of certain metallic oxides, especially the oxides of the alkaline earths. This diminution is due to a very large increase in the electronic emission under the influence of the positive bombardment. Having been led, in this way, to examine numerous oxides from the point of view of their thermionic emission, Wehnelt discovered that, in addition to the oxides of calcium, strontium, and barium, which are much the most active, the oxides of magnesium, zinc, cadmium, thorium, zirconium, etc., also possessed a certain activity. Other oxides, on the contrary (oxides of thallium, aluminium, iron, nickel, cobalt, chromium, copper, etc.), appeared to be completely inactive.

The results of the numerous experiments † which have been made on these 'Wehnelt cathodes' show that the general characteristics of the emission are exactly similar to those which have been given for the emission from

* *Vide* the papers mentioned in the note on page 26, and also Wehnelt and Jentzsch, *Verh. der. Deutsch. Phys. Ges.*, 1908, 10, 605.

† See the bibliography at the beginning of the chapter.

metals. The only difference consists in a greater difficulty of obtaining saturation, but the saturation currents continue to obey Richardson's law:

$$i = aT^{\frac{1}{2}} e^{-\frac{b}{T}}.$$

The difficulty in determining the constants a and b is still greater here than in the previous case. The usual method of making Wehnelt cathodes is, in fact, as follows: a drop of nitrate of calcium strontium, or barium is placed on a wire or thin sheet of platinum; then, by heating the support electrically, the nitrate is evaporated to dryness and calcined, so as to decompose it and obtain the oxide. Under these conditions thermionic emissions are obtained which are very much more intense than those given by pure platinum, but the intensity of the emission changes rather rapidly with the time, doubtless on account of a progressive decomposition or evaporation of the active substance. Nevertheless, it has been possible to obtain fairly concordant values of the constants, and a list of the most probable values is appended:

Oxide	a	b	Authors
Lime.	$6{\cdot}9 \times 10^7$	40,300	Jentzsch, *Ann. der Phys.*, 1908
	$1{\cdot}76 \times 10^7$	43,000	Deininger, *Ann. der Phys.*, 1904
Baryta	$1{\cdot}2 \times 10^7$	45,000	Wehnelt, *Ann. der Phys.*, 1904

Deininger's experiments are particularly instructive. This author found that the emission from lime was independent of the metallic support by means of which it was raised to incandescence. He examined wires of platinum, carbon, tantalum, and nickel from this point of view. This result seems to show that it is a case of an intrinsic

property of the lime and not of a chemical action with the gas or the support.

A large number of oxides other than the oxides of the alkaline earths have been very carefully examined by Jentzsch with respect to their electronic emissions. At relatively low temperatures the majority of these oxides possess an emission greater than that of the platinum which holds them. Under these conditions it is possible to study the law of their emission as a function of the temperature, and to derive the constants of Richardson's formula. On the other hand, at high temperatures the emission from the oxides hitherto examined shows itself to be inferior not only to that from the alkaline earth oxides but even to that from the platinum itself. Thus the effects are to a great extent masked by the characteristic emission from the platinum, and their investigation becomes difficult.

From the theoretical point of view Wehnelt cathodes have given rise to numerous discussions as to whether the mechanism of emission is chemical or intrinsic. The chemical theory has been maintained, in particular, by Fredenhagen* and Horton.† The former attributes the emission to the recombination of the alkaline earth metal with the oxygen liberated by the electrolysis of the oxide. The latter has also established a partial electrolysis of the oxide. Moreover, Fredenhagen has remarked that the oxide gradually disappears during the emission, that the cathode evolves gas continuously, that the underlying platinum is corroded, and that the electronic emission from calcium is strongly increased by the introduction of traces of air into the tube.

But these arguments do not appear to be unanswerable. In the first place, Fredenhagen himself, as well as Horton (who worked with a filament from a Nernst lamp), has

* Fredenhagen, *Ber. der Sachs. Ges. der Wiss.*, 1913, 65, 42; *Phys. Zeits.*, 1914, 15, 21.

† Horton, *Phil. Mag.*, 1906, 11, 505; *Phil. Trans.*, 1914, 214, 277.

established that the oxide has always the same emission at the same temperature, whether the heating be carried out electrically or otherwise. On the other hand, according to Wehnelt and Liebreich,* the loss of oxide can be explained by evaporation combined with the spluttering which arises from the bombardment by the positive ions. Gases are only emitted at the commencement of the heating, and the platinum does not corrode less when it is pure than when it is covered with lime. Finally, according to Horton himself, the lime has an emissive power greatly superior to that of metallic calcium, which explains the influence of traces of oxygen on the emission.

This controversy has lost interest since recent researches have brought to bear such convincing arguments in favour of the intrinsic emission theory that nowadays it appears difficult not to believe in it, in the general case at any rate.

In the first place, Germershausen † has shown that after the last traces of gas have been extracted as completely as possible the emission from Wehnelt cathodes becomes more intense than before, and almost as constant as that from a tungsten filament. Results of much greater importance still have been published recently by Arnold ‡ and his collaborators. The primary aim of this author was to obtain Wehnelt cathodes of as constant an emission as possible, so that a type of three electrode valve could be constructed which should be capable of being used as an interchangeable element in amplifiers for telephone relays. It has been possible to solve this problem in a very satisfactory manner, since the Western Electric Company have been able, by applying Arnold's methods, to manufacture already more than 500,000 valves with Wehnelt cathodes.

* Wehnelt and Liebreich, *Phys. Zeits.*, 1914, 15, 557; *Verh. der. Deutsch. Phys. Ges.*, 1913, 15, 1047.

† Germershausen, *Phys. Zeits.*, 1915, 16, 104.

‡ H. D. Arnold, *Phys. Rev.*, 1920, 16, 70; Davisson and Pidgeon, *Phys. Rev.*, 1920, 15, 553; Davisson and Germer, *Phys. Rev.*, 1920, 15, 330.

The first device employed consists in replacing the pure alkaline earth oxides by mixtures containing two or three of these oxides, the emission from these mixtures greatly exceeding that from the pure oxides. A second improvement lies in the very thoroughly examined choice of metallic support (an alloy of platinum and iridium containing 6 per cent. of iridium), and in the technique of the manufacture of the active layer. This is obtained by suspending the oxides or the carbonates of the alkaline earths in resin or paraffin and applying successive layers of these mixtures to the support. The wire or sheet which serves as the support is heated after each coating so as to carbonize the organic matter and then to burn it off. After a final heating to 1,200° C. there is left a very adhesive layer, which contains two or three milligrams of baryta or strontia per square centimetre of surface, and which, when protected from moisture and carbon dioxide, can be kept without deterioration for several years.

All the advances which have been realized in vacuum technique are used in the evacuation of the electronic emission tubes constructed with these filaments, and vacua of the order of 10^{-7} and 10^{-9} microns of mercury are produced. In this way large and perfectly regular emissions are obtained, whereby the constants of Richardson's formula can be determined. The values of the constant a have been found to vary according to the oxide content of the filament, between 8×10^4 and 24×10^4. The constant b varies from 19,400 to 23,800, and is appreciably smaller, therefore, than for pure metals, this corresponding to an appreciable increase in the emissive power. Traces of gas exercising a pressure of less than a micron of mercury may have a strong influence on the emission (we shall see later that this is also true in the case of pure metals). Oxygen and carbon dioxide diminish the currents yielded in very great proportions, whilst hydrogen augments them.

Some very curious facts have been observed whilst

heating a plate covered with oxide in the neighbourhood of a bare metallic plate in a good vacuum. In this way a very small quantity of oxide can be distilled over on to the pure metal, a quantity which can be estimated by various methods. By this means it is possible to examine how the emissive power of a metallic plate at a given temperature varies with the thickness of the layer of oxide which covers it. The result is as follows : it is sufficient to deposit a *monomolecular* film of lime on about one-third of the surface of the metal for the emissive power to become approximately equal to that of the oxide. It has even been established that if the thickness of the oxide is progressively increased the emission commences by increasing very rapidly to a value very much higher than that which corresponds to either the metal or to the oxide, and then soon declines to a value which corresponds to that for the solid oxide. This is a very striking example of the extreme sensitivity of thermionic phenomena to the least traces of superficial impurities. The molecules of oxide deposited on the filament seem to act as valves which facilitate the exit of the electrons contained in the metal, without having any direct chemical action. Another fact which supports the same idea is that if the emission by a filament covered with a trace of oxide is prolonged for a sufficient period (several hours), the total weight of the electrons collected ultimately exceeds twenty or thirty times the actual weight of the oxide. It appears difficult to interpret this fact on a theory having recourse to chemical actions.

Finally, it should be mentioned that Arnold has sometimes accidentally observed emissions which are very much stronger than those normally yielded by the mixtures of oxides of the alkaline earths. Perhaps these emissions may be due to fortuitous mixtures of impurities with the normal oxides. This should lead to the systematic examination of mixtures of refractory materials ; it is not impossible that this might result in the discovery of

substances which are still more active than those at present in use.

To complete the study of Wehnelt cathodes it is important to notice that they lend themselves with a particular facility to the production of beams of intense and almost homogeneous cathode rays. In fact, if a very small spot of lime is placed on a platinum strip and raised to red heat in a vacuum, it is possible to realize conditions such that the emission from the metal is entirely negligible compared with that from the oxide, so that in practice it can be considered that only the latter emits electrons. It then becomes possible to subject the cathode rays produced to a magnetic field under conditions such that the magnetic action can be separated completely from the electric action which gives rise to the rays. With a suitably oriented magnetic field the cathode rays describe a circular path, and the determination of the radius of this path enables the ratio of e/m for the particles in motion to be calculated by the classical formulae. This method of measuring e/m, for the detailed account of which reference should be made to the original papers, was proposed by Wehnelt,* but improved by Bestelmeyer.† The latter obtained the number $1{\cdot}766 \times 10^7$ electromagnetic units, and this value appears to be accurate to within one-half of one per cent. In addition, it is in very satisfactory agreement with all the values obtained by the other, very different, methods, so that the identity of the particles which carry the negative thermionic current in a vacuum with the cathodic corpuscles can no longer be doubted.

* Wehnelt, *Ann. der Phys.*, 1904, 14, 425.
† Bestelmeyer, *Ann. der Phys.*, 1911, 35, 909.

CHAPTER V

THE DISTRIBUTION OF VELOCITIES AND THE EXCHANGES OF ENERGY IN ELECTRONIC EMISSION

IN the previous chapters it has been assumed that the electrons emitted at a given temperature in a vacuum by an incandescent metal form an electronic gas outside the metal which has all the properties of a perfect gas. Its particles have velocities distributed about their mean value according to Maxwell's law, and this mean value can be calculated by the same methods as for a molecule of a perfect gas at the same temperature, using the classical formulae of the kinetic theory. These hypotheses, on which have been built the theoretical arguments of Chapter III, can be justified, as we have seen on page 17, by qualitative considerations of a general nature. But it is more satisfactory to subject them to verification by direct experiment. This task has been undertaken and brought to a successful conclusion by Richardson and his students, and we will summarize briefly the methods which they have employed.

If the formulae of the kinetic theory * be assumed and if n be used to denote the total number of electrons emitted per unit time and unit surface, and if n_1 of these have a velocity component normal to the surface between u and $u+du$, and n_2 and n_3 have tangential components between v and $v+dv$ and w and $w+dw$ respectively, then

* For the details of these formulae and of the calculations reference should be made to the following books : Eugène Bloch, *Kinetic Theory of Gases* ; Richardson, *Emission*, p. 156 et seq.

$$\left.\begin{aligned} n_1 &= n \times 2hmue^{-hmu^2}\, du \\ n_2 &= n\sqrt{\frac{hm}{\pi}}\, e^{-hmv^2}\, dv \\ n_3 &= n\sqrt{\frac{hm}{\pi}}\, e^{-hmw^2}\, dw \end{aligned}\right\} \quad \ldots\ldots\ldots (16)$$

In these expressions, m represents, as before, the mass of an electron, and h is related to the absolute temperature by the formula already used

$$h = \frac{1}{2k\mathrm{T}} \quad \ldots\ldots\ldots\ldots\ldots (17)$$

It may be observed, in passing, that according to the expressions (16) the mean kinetic energy of an emitted electron is $2k\mathrm{T}$ and not $\frac{3k\mathrm{T}}{2}$, as is that of a gas molecule in thermal equilibrium at the same temperature. This is due to the fact that large velocities are more frequent in a current of emitted electrons than in a system of electrons in statistical equilibrium at a given temperature.

1. The distribution of the normal components of the velocities. The first of the equations (16) was initially verified by Richardson and Brown.* The apparatus employed is shown in Fig. 7. It consists of a thin plane condenser, of which the upper armature U is connected to an electrometer and collects the electrons emitted normally by the platinum strip H, raised to incandescence in a vacuum. This strip is in the same plane as the lower electrode L in order to ensure as uniform a field as possible.

If the lower armature is at the same potential as the upper, or at a lower potential, the electrons emitted will

* Richardson and Brown, *Phil. Mag.*, 1908, 16, 353.

easily arrive at U. If on the contrary, an increasing and opposing potential difference be established between the two armatures (the incandescent strip being positive with

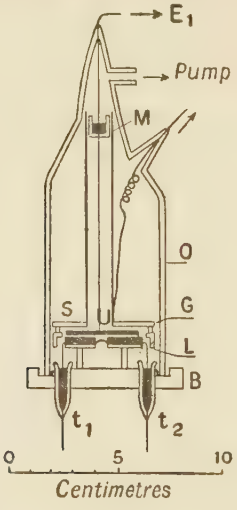

FIG. 7

respect to the upper armature), the current received by the electrometer will progressively diminish, and an easy calculation shows that it is related to the opposing potential difference V by the equation

$$\log \frac{i}{i_o} = -\frac{Ne}{RT}V, \quad \ldots\ldots\ldots\ldots (18)$$

in which N and R represent, as before, Avogadro's number and the perfect gas constant with respect to a gramme-molecule, and i_o is the initial current when the field is zero.

The results of one experiment are shown in Fig. 8, the potential differences V being plotted as abscissae and the

currents i as ordinates. The results are also plotted on the same graph with the logarithms of the currents as ordinates. It is seen that the exponential law (18) is very approximately verified. Moreover, the slope of the line obtained is definite, and from it the value of the perfect gas constant R must be calculable. Now, a large number of experiments have yielded numerical values comprised

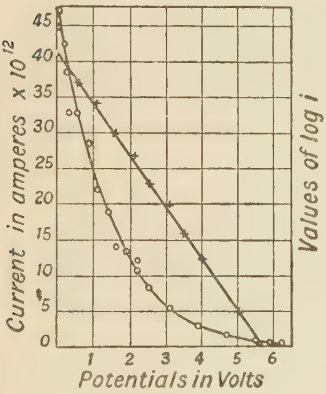

FIG. 8

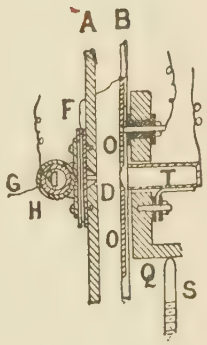

FIG. 9

between $6{\cdot}9 \times 10^7$ and 10×10^7, and the mean of these, equal to $8{\cdot}34 \times 10^7$, by a fortunate coincidence, happens to be exceedingly near to the theoretical number $8{\cdot}32 \times 10^7$.

2. The distribution of the tangential components. The investigations of the distribution of the tangential components, also carried out by Richardson,* affords more complete information than the above. The apparatus employed is shown in section in Fig. 9. The two parallel plates A and B are each furnished with a medial slit (perpendicular to the plane of the figure). The first is closed by a sheet of platinum D which can be made red hot in

* Richardson, *Phil. Mag.*, 1908, 16, 890; 1909, 18, 681.

the vacuum. An accelerating electric field carries the electrons emitted towards the second plate and some of them penetrate, through the second slit, into a Faraday cylinder T placed behind it and connected to a sensitive electrometer. A micrometer screw, the point S of which can be seen in the figure, allows the plate B to be displaced in its own plane, moving the Faraday cylinder which is rigidly attached to it. In this way it is possible to collect successively the electrons emitted normally and obliquely by the heated strip, and by a suitable arrangement of the electrometer to compare the total current received by the whole of the plate B with these partial currents.

If the electrons emitted did not possess initial velocities, the least accelerating field would direct them all normally to the plate B, so that the currents received by the Faraday cylinder would only have an appreciable intensity when the slit of the plate B was exactly opposite the incandescent strip. Actually this is not the case, and if a curve be drawn with the distances of the slit from its initial position as abscissae and the currents measured by the electrometer as ordinates, the law of the distribution of the tangential velocities among the electrons emitted, can be deduced from its shape. It is found that the qualitative and quantitative agreement with Maxwell's law (the second and third of the expressions 16) is satisfactory, especially if the accelerating potential is not too great.

Several disturbing effects combine to diminish the accuracy which can be expected from experiments of this nature. In the first place, if the electronic emission becomes too great it is no longer possible to neglect, as we have done hitherto, the mutual repulsion between the electrons. The calculations become much more complicated and the correction is difficult. Similar calculations have been made by Schottky * in the case of a cold cylindrical electrode surrounding an incandescent cylindrical wire, and they appear to be verified by experiment.

* Schottky, *Ann. der Phys.*, 1914, 44, 1011.

Moreover, it seems that in Richardson's experiments the currents emitted remained so small that the correction was hardly necessary. But we shall see in the following chapter that the phenomenon of the mutual repulsion of the electrons may, in other cases, assume an altogether preponderating influence.

A second cause of error resides in the partial reflection to which the electrons are liable when they strike the plate B, and it is difficult to estimate the exact importance of this. From Richardson's work and also from some experiments by von Baeyer * it appears that the electrons of very low velocity may be reflected in the proportion of thirty per cent in some cases. This would render the interpretation of some measurements much less easy.

Finally, the fall of potential along the filament, which is involved by the heating current, also introduces important disturbances when the accelerating field is small. Both von Baeyer, and after him Schottky, have been led to make the heating current pass intermittently and to connect the electrode receiving the electrons to the electrometer during the intervals when the heating current was not flowing. This end is achieved by means of a rotating commutator, and entirely eliminates the cause of error mentioned. Further reference to this point will be made in Chapter VI.

The experiments carried out by S. L. Ting,† one of Richardson's students, seem to prove that the law of distribution of velocities in electronic emission is in need of revision. This author, working with platinum and tungsten, has established that Maxwell's law is certainly satisfied, but that in general the mean velocity of the electrons emitted is greater than that which would be calculated from the temperature of the filament ; it would correspond to a temperature about double that observed.

* von Baeyer, *Verh. der Deutsch. Phys. Ges.*, 1908, 10, 96 and 953 ; *Phys., Zeits.* ; 1909, 10, 168.

† S. L. Ting, *Proc. Roy. Soc.*, 1921, 98, 374.

This still unexplained fact would seem to merit further investigation. However this may be, one important result appears to emerge from all these measurements : the distribution of the velocities of the electrons outside the metal satisfies Maxwell's law. This is the first time that this law has been directly verified in detail and not solely by the measurement of a mean velocity. The possibility of such a verification arises from the fact that the particles examined carry electric charges and that the sensitivity of electrometric measurements is very high.

3. The latent heat of evaporation of the electrons. It was stated in the first paragraph of this chapter that the mean kinetic energy of an electron emitted by a metal at a temperature T is equal to $2k\mathrm{T}$. On the other hand, we have introduced into our arguments in Chapter III the work necessary to extract an electron from a metal at the same temperature, a quantity which has been denoted by φ. Thus, when an electron escapes from a metal it has to be given, on the average, an energy equal to $\varphi + 2k\mathrm{T}$, and if the saturation current received per square centimetre is i, then the total energy which has had to be communicated to the electrons which constitute it will be

$$\mathrm{W} = \frac{i}{e}(\varphi + 2k\mathrm{T}) = i\left(\mathrm{V} + \frac{2\mathrm{R}}{\mathrm{N}e}\mathrm{T}\right), \ldots\ldots (19)$$

assuming that the work of extraction φ is equal to that which is necessary to overcome a fall of potential V. This energy can be compared with the latent heat of evaporation of a liquid, and, indeed, we have already been led in Chapter III to introduce this conception into our thermodynamical arguments (the kinetic energy of the electrons emitted being then neglected).

As the current due to electronic emission increases extremely rapidly with the temperature, the formula (19) shows that the latent heat in question also rises very

rapidly, and a simple calculation shows that it must be very appreciable at easily accessible temperatures. It is reasonable, therefore, to propose to obtain evidence of it by direct experiments. The formula (19) shows that if this is successful there will result at the same time a new method of determining the contact potential differences between metals and vacuum, which already play such an important part in Richardson's formula.

The first attempt to demonstrate this effect was made by Wehnelt and Jentzsch.* These authors employed a Wehnelt cathode heated in vacuo and forming one arm of a Wheatstone's bridge. If the resistance at the temperature of the experiment is ρ, and the heating current is I, it will be necessary at the moment when the filament is negatively charged and commences to emit electrons, to increase the heating current to the value $I + dI$ in order to maintain the temperature of the filament constant in spite of the loss of energy W. Equating this supplementary electrical energy thus communicated to the filament to the energy corresponding to the latent heat of evaporation of the electrons, it is easy to obtain the relation

$$2\rho\, I\, dI = i\left[V + \frac{2R}{N\bar{e}}(T - T_0)\right].$$

The term T_0 has been introduced to take account of the fact that the electrons emitted by the filament at the temperature T have reached there through the cold ends of the circuit which are at the temperature T_0.

The preceding formula, in which all the quantities can be determined experimentally except V, enables this difference of potential to be calculated, and consequently the results can be compared with those which have been deduced from Richardson's formula. Unfortunately the

* Wehnelt and Jentzsch, *Verh. der Deutsch. Phys. Ges.*, 1908, 10, 610; *Ann. der Phys.*, 1909, 28, 537.

experiments are very difficult to carry out and great precautions and rather numerous corrections are necessary. In fact, it is necessary to take into account the action of the thermionic current itself on the galvanometer used for establishing the equilibrium of the Wheatstone's bridge, and also the alteration of the distribution of the temperatures along the filament which is due to the same cause. Finally, it is necessary to work in a vacuum so high that no ionization of the residual gas by collision of the electrons is to be feared. Unless this is done the positive ions received by the filament can give up to it sufficient heat to mask the cooling due to the electron emission.

These precautions were only taken completely for the first time in the experiments of Richardson and Cooke,* who worked with osmium filaments and later with tungsten filaments. The values obtained for V have a mean value of 4·7 volts for osmium and 4·63 volts for tungsten. From these the values of the constants b in formula (6) (page 15) are ascertained to be 54,000 and 56,200. These values are in satisfactory agreement with those deduced from Richardson's law (see the table on page 33).

The difficult examination of Wehnelt cathodes has been re-undertaken from the modern point of view in a whole series of experiments by Cooke and Richardson,† Wehnelt and Liebreich,‡ and most recently by W. Wilson.§ Using the Wehnelt cathodes investigated by the Western Electric Company, the properties of which have been given on page 39, the last named has been able to obtain entirely consistent results. With the same cathodes he has measured the latent heats of evaporation and the constants of Richardson's formula. The values of the contact potential differences deduced from the two series of measurements agree very well, as is shown by the table on page 51.

* Richardson and Cooke, *Phil. Mag.*, 1913, 25, 628.
† Cooke and Richardson, *Phil. Mag.*, 1913, 26, 472.
‡ Wehnelt and Liebreich, *Phys. Zeits.*, 1914, 15, 548.
§ W. Wilson, mentioned by Arnold, *Phys. Rev.*, 1920, 26, 78. See also *Proc. Nat. Acad. Science*, 1917, 3, 426.

Lester * has also examined molybdenum, carbon, tantalum, and tungsten by the method of Richardson and Cooke. The values of the contact potential difference between the metal and vacuum deduced from these measurements of the latent heats are as follow :

4·588, 4·55, 4·511, 4·478.

These are so nearly the same as to raise the question whether they are not in reality exactly equal to one another. Moreover, the same comment has already been excited by the results in the table on page 33, which were obtained

Composition of the Oxide	V Deduced from Richardson's Formula	V Deduced from the Latent Heat
BaO 50 per cent, SrO 50 per cent.	2·02	1·97
	2·16	2·28
Ba 50 per cent, SrO 25 per cent, CaO 25 per cent . .	2·34	2·39
	2·59	2·54
CaO	3·28	3·22
	3·49	3·51

in the investigation of Richardson's law. If this equality of potentials should be confirmed in the future it will have to be concluded, as has been remarked on page 25, that the contact differences of potential in a vacuum between any two metals in the preceding list is zero.

4. The heat liberated in the absorption of electrons. It has been known for a long time that the electrons emitted by a metal can acquire, under the action of an electric field, a kinetic energy sufficiently great to cause a metallic electrode to be raised to a very high temperature by their impact on it. But even if the electrons reach the metallic

* Lester, *Phil. Mag.*, 1916, 31, 197.

surface with zero velocity they will liberate a certain amount of energy in passing through the surface to enter the metal, and this will result in a heating of the metal which may be used to give a measure of the work done. This phenomenon, the converse of the preceding one and comparable with the liberation of heat which accompanies the condensation of a gas into the liquid state, is capable of furnishing a new method of measuring the contact potential difference between the metal and the surrounding medium.

This experiment has been carried out by Cooke and Richardson.* An osmium filament was heated in a vacuum in the neighbourhood of a cold metallic plate, and a small difference of potential was established between the two which was just sufficient to allow the electrons to reach the plate. The heat liberated in the latter was determined by measuring the variations of its resistance using a Wheatstone's bridge method. Here again great precautions are necessary in order to take into account the possible disturbance of the equilibrium of the bridge by the thermionic current itself and also of the Joule effect of this current. Finally, as the difference of potential applied to the system in order to collect the electrons cannot be zero, it is necessary to work with small and decreasing tensions and to extrapolate the curve obtained to the limit which would correspond to a zero tension. Obviously, also, account will have to be taken of the contact potential difference, which leads to yet another correction.

The results of such difficult measurements cannot pretend to great accuracy. Nevertheless, it is remarkable that the values of the contact potential differences which are deduced from these measurements agree in a satisfactory manner with those which have been obtained from the investigation of the latent heat of vaporization.

It would be interesting to have these experiments repeated with tungsten filaments, making use of all the advances in vacuum technique.

* Cooke and Richardson *Phil. Mag.*, 1910, 20, 173 ; 1911, 21, 404.

CHAPTER VI

THE SATURATION CURVES IN PURE ELECTRONIC EMISSION

1. Introduction. In the preceding chapters we have always assumed that the electronic currents measured were saturation currents, i.e. that the difference of potential established between the cathode and the anode was sufficient to collect all the electrons emitted.

At first sight this hypothesis does not appear to cause any difficulty. Let us suppose, for example, that the cathode is an incandescent filament lying along the axis of a concentric cylindrical anode, an arrangement which we know to have been frequently adopted. Let us neglect the velocities of emission of the electrons so that they may be considered as almost motionless particles in the neighbourhood of the incandescent filament. It is clear that the least excess of the potential of the cylinder over that of the filament will start the electrons moving towards the cylinder, and that they will all arrive there provided that there are not so many of them that they exercise mutual actions on one another, and provided also that the vacuum is sufficiently high for none of them to be turned out of its path by collision with the molecules of the gas. In this case the current measured must be the saturation current.

This conclusion is true *a fortiori* if the initial velocities of the electrons are no longer negligible. Whatever may be the direction of the initial velocities the electrons will be carried over to the external cylinder, and will arrive there even if there is no difference of potential between the two electrodes. More than this, saturation must still be nearly attained when a weak, opposing field is established between the electrodes, which only stops the slowest

electrons. It should be noted, in passing, that in the evaluation of this field, or, more generally, in the evaluation of a small difference of potential between the two electrodes, it is necessary to take into account the contact difference of potential if there be one. It is after this difference has been compensated by a potentiometer method that the weak fields in question are applied.

Finally, it is seen that in the case of a cylindrical field the electronic current must be the saturation current itself, even when the field is very nearly zero. If the field is no longer cylindrical—for example, if an incandescent filament is placed in the neighbourhood of a plane sheet—this conclusion may be slightly modified, at any rate in the case where the velocities of emission are not neglected. As these velocities are in all directions, it is conceivable that an appreciable number of the electrons may be able to escape from the field and will fail to arrive at the cold electrode when the potential of this is not sufficiently great. To obtain some idea of the importance of this effect let us recall that the velocities of emission of the electrons are distributed about the mean velocity according to Maxwell's distribution law, and that the mean kinetic energy of the electrons emitted at a temperature T is $2kT$. It is very easy to calculate from this the velocities at any given temperature, or, which comes to the same thing, to ascertain the differences of potential which the electrons are capable of surmounting. It is found that at a temperature of 2,400 degrees absolute, the temperature commonly reached in tungsten filament lamps, only 50 per cent of the electrons are capable of overcoming a difference of potential of 0·143 volts. In short, an opposing potential difference of a few tenths of a volt is sufficient, at this temperature, to stop practically all the electrons. The same holds to an even greater extent at lower temperatures. Again, it can be said that by establishing a potential difference of a few volts, about ten, for example, between the anode and the cathode, the resulting field will

be large enough in all cases to overcome the initial velocities of the electrons and to carry them towards the anode. Thus it can be predicted that even when the geometrical arrangement of the electrodes is not very favourable to saturation, this can nevertheless be attained as soon as the voltage applied exceeds ten volts.

These predictions appeared to have been confirmed experimentally in all the earlier thermionic researches, and the authors who had occasion to consider this question found in it no difficulty whatsoever. The situation has changed since valves with tungsten filament have enabled us to operate at higher temperatures than had been in use previously, and to obtain electronic emissions measured not in microamperes but in milliamperes or in tens of milliamperes. The intensity of such emissions has enabled us to observe certain facts which are apparently quite paradoxical, and which it has been possible to explain only by a very careful reconsideration of the conditions of saturation.

2. The 3/2 power law. Certain facts formerly known and observable with ordinary incandescent filament lamps having refractory filaments (carbon and tungsten) could not easily be interpreted on the theories current at the time they were discovered. If a lamp of this type is fed with continuous current, at a voltage of 110 volts, for example, a current of the order of 0·5 amperes will pass through it, and the temperature of the filament will be of the order of 2,000 degrees. The power furnished by the supply must provide not only for the heating of the filament but also for the electronic current which necessarily passes in the vacuum of the lamp between the extreme positive and extreme negative ends of the filament. This latter current is not very large at 2,000 degrees, but if the applied voltage be increased slowly so that the temperature of the filament is raised to 3,000 degrees, Richardson's formula, the constants of which are fairly accurately known for

tungsten, leads to the prediction of such an increase in the electronic current that the current supplied to the lamp must have a value very much greater than that which is actually measured experimentally. This increase, instead of being of the order of one- or two-tenths of an ampere, should attain an ampere or even more in some cases. This apparent contradiction between experiment and Richardson's formula is very soon explained if it be supposed that the difference of potential of the order of 100 volts which gives rise to the passage of the electronic current is quite insufficient to saturate this current, and if Richardson's formula consequently becomes inapplicable to the case.

The study of these paradoxical facts, to which others have since been added, led Langmuir to undertake a detailed re-examination of the saturation curves and of the mechanism of this saturation. In this way he arrived at some general conclusions of great importance, which will be examined in some detail.

Let us first state an experimental result, initially announced by Lilienfeld * but completely investigated by Langmuir.† If a fixed potential difference of say 100 volts is applied between a tungsten cathode raised to a high temperature and a cold anode, and the curve constructed which represents the current received as a function of the temperature, it might be expected that the classical curve of Richardson would be obtained, and this actually would be the case if saturation were always realized. Experiment shows that in reality the current, after having commenced to increase in accordance with Richardson's law, ends by departing from this law, assuming values less than the theoretical values and at high temperatures becoming *rigorously constant.* This result is easily visible in the curves of Fig. 10 taken from Langmuir's paper. The dotted curves represent the currents collected at different

* Lilienfeld, *Ann. der Phys.*, 1910, 32, 673 ; *Leipzig Ber.*, 1911, 63, 534.

† Langmuir, *Phys. Rev.*, 1913, 2, 453 ; *Langmuir's Record, passim.*

temperatures with fixed voltages, namely, 60, 120, and 240 volts. The continuous curve represents Richardson's law. Thus, above a certain temperature the current which can be extracted from the vacuum with a definite applied voltage is itself fixed. Whatever the number of electrons which the filament may be caused to emit, it is impossible by varying the voltage to extract from the filament more than a certain definite current, governed at first by the voltage but afterwards by the geometrical arrangement of

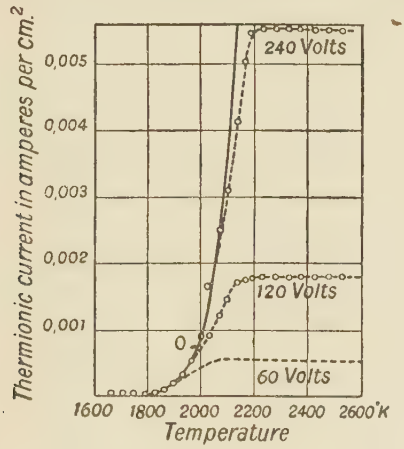

FIG. 10

the electrodes. All the other electrons are led back towards the cathode by a process which will be elucidated.

The explanation of Langmuir's curves must be sought in the mutual repulsion of the electrons emitted by the filament. This repulsion, which is negligible when the number of electrons is so small that the current does not exceed a small fraction of a milliampere, becomes, on the contrary, very considerable when the temperature of the filament is high enough for the electronic current to be greater than a milliampere. In this latter case there

exists in the space between the electrodes a negative charge, the density of which is very appreciable. The field of mutual repulsion which results therefrom is superposed on the accelerating field so that saturation becomes more difficult. As the temperature of the filament is increased there comes a time when the space charge is such that the field it produces sends back to the cathode all the electrons which leave it; after this the current shows no further increase, whatever the temperature of the filament.

To define further the mechanism which has just been outlined, let us examine the particular case of an incandescent plane cathode of infinite extent placed parallel to a cold anode which is also plane and infinite. Let a uniform field be set up between these two electrodes, which are assumed to be in a vacuum, by establishing between them a potential difference V; the potential of the incandescent cathode will be taken as zero. The electrons emitted by the cathode create a density ρ of negative charges in the space between the plates, and this destroys the uniformity of the field. If a line perpendicular to the two plates be taken as the axis of X and its point of intersection O with the heated plate as origin (Fig. 11), then the potential at any point between the plates will be given by Poisson's equation

$$\frac{d^2V}{dx^2} = -4\pi\rho \quad \ldots\ldots\ldots\ldots (20)$$

So long as ρ is small the second member of the equation can be neglected and the potential distribution remains linear; it can be represented by the straight line OA. When ρ is no longer negligible the equation (20) shows that the curve which represents V as a function of x must be concave upwards, as is the curve OMA in the figure. This deformation of the law of potential distribution will be accentuated as the density of the negative charges increases, and eventually the curve will become tangential to the axis

of x at the origin (curve OM'A in the figure). The current which the difference of potential V has caused to pass between the plates and which, up to this point, has continually increased, now ceases to grow larger since the field in the vicinity of the cathode has become zero, and consequently no longer tends to make the electrons move towards the anode, provided always that the initial velocity of the electrons can be neglected.

By making use of a theory which was given in its first form by J. J. Thomson* and developed by Child,† it is

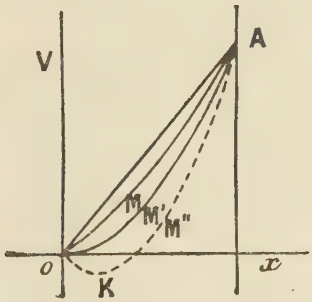

FIG. 11

easy to complete this qualitative explanation by an exact calculation. In fact, let us ascertain the relation between the current i and the potential difference V from the time when the current has assumed its limiting value. If the initial electronic velocities be neglected, the velocity v possessed by an electron having a charge e (in absolute units), at a point where the potential exceeds that of the heated plate by V, is given by the equation

$$\tfrac{1}{2}mv^2 = Ve \ldots\ldots\ldots\ldots\ldots\ldots (21)$$

If ρ is the *absolute value* of the density of the space charge

* J. J. Thomson, *Conduction of Electricity through Gases*, p. 223.
† Child, *Phys. Rev.*, 1911, 32, 498.

at the point considered, the current will be given by the relation

$$i = \rho v, \quad \ldots\ldots\ldots\ldots\ldots (22)$$

with the condition

$$\frac{d^2V}{dx^2} = 4\pi\rho \quad \ldots\ldots\ldots\ldots\ldots\ldots (23)$$

The elimination of ρ and v gives

$$\frac{d^2V}{dx^2} = 4\pi i \sqrt{\frac{m}{2Ve}},$$

and, by observing that $\frac{dV}{dx}$ vanishes when $V = 0$,

$$\left(\frac{dV}{dx}\right)^2 = 8\pi i \sqrt{\frac{2mV}{e}}.$$

Integrating a second time and making V vanish when $x = 0$, we finally get the formula

$$i = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{x^2}, \quad \ldots\ldots\ldots\ldots\ldots (24)$$

in which x represents the distance between the two plates. It will be seen that the current increases proportionally to the 3/2 power of the applied voltage, the constant involved in the proportionality depending only on the ratio e/m and on the distance between the two plates.

It is obvious that it will not be very easy to obtain a uniform field in quantitative experiments which might be undertaken to verify this relation, but Langmuir has been able to repeat the calculation in the case of a cylindrical field created between an interior heated electrode and a

cold external electrode. The formula obtained, in a manner similar to the foregoing, is

$$i = \frac{2\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{\beta^2 r}, \quad \ldots\ldots\ldots\ldots\ldots (25)$$

where r is the radius of the external cylinder and β is given by

$$\beta = \log\frac{r}{a} - \frac{2}{5}\left(\log\frac{r}{a}\right)^2 + \frac{11}{120}\left(\log\frac{r}{a}\right)^3 - \frac{47}{3300}\left(\log\frac{r}{a}\right)^4 + \ldots$$

In this series a represents the radius of the heated wire. The coefficient β rapidly tends towards unity as the ratio r/a increases, and if the radius of the cylinder attains about twenty times that of the wire the error introduced by replacing β by unity becomes less than one per cent.

The formula (25) can be more easily verified quantitatively than the formula (24) ; in fact, it is fairly easy to obtain a cylindrical field of the type indicated. Dushman* heated a tungsten filament stretched along the axis of a molybdenum cylinder, the latter being prolonged on either side by two cylinders of the same diameter, forming a kind of guard ring. In this way he was able to verify with great accuracy the proportionality of the current to the 3/2 power of the voltage. Knowing the coefficient of proportionality and the radius of the external cylinder, the ratio e/m for the electrons which carry the charges can be calculated from the formula (25). The value obtained was $1{\cdot}755 \times 10^7$ electromagnetic units. It will be observed that the agreement of this with the value usually accepted is very satisfactory, and this confirmation of Langmuir's theory is very valuable. It is even conceivable that the foregoing experiment might be adopted as a new precision method for determining the ratio e/m.

* Dushman, *Phys. Rev.*, 1914, 4, 121.

Langmuir has shown that the law

$$i = kV^{\frac{3}{2}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (26)$$

which expresses the proportionality of the current to the 3/2 power of the applied voltage, derived by the theory for a uniform field and for a cylindrical field, and subsequently verified in the latter case, still holds good for any field of any shape whatsoever, provided that the electronic emission is sufficiently intense to call into play the mechanism of the mutual repulsion of the electrons of the space charge. A large number of experimental verifications have been carried out using tubes with differently arranged electrodes, and the reason why the 3/2 power law should remain valid can be seen also from very simple dimensional considerations. The formulae (21) and (22) are true in all cases. If, in them, the voltage V be multiplied by an arbitrary factor p, and the current i by the factor $p^{\frac{3}{2}}$, the elimination of v between the two equations gives

$$\rho = -pi\sqrt{\frac{m}{2Ve}},$$

which shows that the density ρ has been multiplied by the factor p. These two magnitudes, therefore, will still be related by Poisson's general equation

$$\triangle V = 4\pi\rho.$$

Thus the 3/2 power law seems to govern in a perfectly general manner the phenomena of the carriage of current by electrons before the saturation stage is reached.

Before we leave these theoretical considerations it is important to remark that we have neglected explicitly the initial velocities of the electrons in arriving at formulae

(24) and (25). What correction will have to be made in order to take account of these velocities? A complete answer to this question necessitates rather complex calculations, but it is not difficult to indicate qualitatively the form the correction must take. In fact, if the electrons have an initial velocity which is not zero in the direction of the axis of x (Fig. 11), then when the electric field at the heated electrode becomes zero (curve OM'A) the electrons will still be able to attain to a region some distance from the electrode where the field will not be zero, and consequently they will be in a position to be carried towards the anode; the maximum current will not yet have been reached. It will be possible for the density of the electric charges in the space between the plates to continue to grow, and the curve showing the potential distribution will be able to assume a form still more concave, similar to the curve OM''A which is shown dotted in Fig. 11. It is seen that in this case the field in contact with the cathode will be in a direction opposite to that obtaining in the anodic region, and that the point K for which the potential is a minimum and the field zero has been moved to some distance from the cathode. It is when the opposing fall of potential thus created between the cathode and the point K of minimum potential has become large enough to stop practically all the electrons emitted by the cathode that the current will be unable to grow any larger, and that the flat part of the curve in Fig. 10 will be reached.

As the assumptions which form the basis of the theory developed above are now fulfilled between the point K of the curve, corresponding to the minimum voltage, and the point A, corresponding to the anode, the formula (24) will continue to apply on condition that V is employed to denote the potential difference between the points A and K (a difference a little greater than the applied voltage) and x to denote the distance between the point K and the anode (a distance a little less than that between the plates).

It has been previously noticed that the velocities of

emission of the electrons correspond, on the average, to that acquired under the influence of a fall of potential of a few tenths of a volt at the most. If, therefore the voltage applied to the anode is sufficient, for example, if it is 100 volts, the portion of the curve OM''A between the origin and the minimum K will be compressed into a very small distance in the neighbourhood of the origin, and the potential minimum itself will be only slightly less than zero. In other words, the correction to be made to the preceding formulae will be insignificant. In general, therefore, it will not be necessary to take it into account, unless, for example, it is proposed to make an accurate determination of the ratio e/m in absolute units.

3. Other obstacles to saturation. We have just examined in detail the principal cause which prevents the saturation of electronic currents, namely, the space charge created by the electrons as soon as the thermionic current is sufficiently intense, and the mutual repulsion which this space charge entails. But in addition to this fundamental cause there are several others which may play important parts in certain cases.

One of these which has been known for a very long time consists in the want of homogeneity of the filament. If the irregularities in the incandescent filament are such that the electronic emission has not the same value at neighbouring points in it, local differences of potential will be established between these points, and the electric fields which result thereform will again act as opposing fields with respect to the principal accelerating field which directs the electrons towards the anode. Saturation will only be attained when the applied voltage predominates over the local fields.

In the same connexion it can be shown that the introduction into the tube of a conductor, or of any insulator whatever carrying any electric charge which is not zero, will create a field capable of interfering with the principal

field. This supplementary field will be able to deflect some of the electrons from their normal path and thus delay saturation. This case arises in particular in certain tubes in which the cold anode and the incandescent cathode are separated by a distance much greater than their own dimensions. Some of the electrons emitted by the cathode can reach the glass walls of the tube and accumulate there to such an extent that the repulsion which they exert on the electrons subsequently emitted completely changes the laws under which the tube functions. This explains several apparently paradoxical facts which have been announced on various occasions (see *Langmuir's Record*). It also enables us to understand why several investigators have thought they observed a considerable *diminution* in the electronic currents when the vacuum was improved: this apparent diminution being due to an increasing charge on the walls of the tube, and not, as was thought, to the decrease of certain chemical actions due to the residual gas.

Another example of the same type is furnished by the Coolidge tube for the production of X-rays. It is well known that in this tube the incandescent cathode is surrounded by an annular electrode which is not heated but which is raised to the same potential, the shape being so chosen that the electrons emitted by the cathode converge on to the anticathode with greater accuracy. The presence of this supplementary conductor prevents the 3/2 power law applying to the Coolidge tube, though it does apply when the additional electrode is absent. This result implies a disturbance of the law of saturation which is easily interpreted after what has been said.

When the saturation law is disturbed in this way by a supplementary conductor raised to a suitable potential, the tube in question becomes a three electrode tube or valve, the anode serving as the 'plate', and the auxiliary conductor as the 'grid', to employ the usual terminology. Thus all the effects which retard saturation that we have just considered can be grouped together under the title

grid effects produced by the action of certain parts of the system on the other parts.

Finally, a last obstacle to saturation is to be found in the filament heating current itself. Moreover, this current is involved in two ways, both prejudicial to saturation. In the first place, there exists along the filament (which is assumed to be heated by a battery of accumulators) a fall of potential which in many cases attains several volts (from four to twenty). If the voltage applied to the anode is reckoned from the negative extremity of the filament, it is evident that when it is small it will commence by extracting an electronic current from the negative end but will not be able to do so from the positive end till its value exceeds the potential at this end. Thus, even if the partial currents extracted at each instant are saturated there will be a gradual increase of the whole as the voltage is increased which will mask completely the true saturation. Similarly, if the partial currents collected by the anode are still in the phase preceding saturation, where they satisfy the 3/2 power law, this law will also be obscured by the apparent supplementary increase due to the same cause. This latter case obtains in practice with strongly heated tungsten filaments if the cylindrical anode is at a potential which does not exceed that of the positive end of the filament. In this case the current passing to the anode from those parts of the filament which are at a potential lower than that of the anode (the only parts active in the experiment) is proportional to the 3/2 power of the anodic potential. On the other hand, the part of the heated filament capable of sending electrons to the anode has a length which obviously increases in direct proportion to the potential of the latter. It follows that the total current received will be proportional to the 5/2 power of the applied voltage instead of to the 3/2 power.

The heating current also hinders saturation by another process: it produces in its neighbourhood a magnetic field which causes the paths of the electrons to become

curved and so prevents them from reaching the anode directly. It is evident that this action further contributes to raising the potential necessary to obtain saturation.

The experiments of von Baeyer and Schottky already mentioned (page 47) have shown that the effects arising from the heating current can be eliminated completely by using an intermittent heating current and measuring the electronic current in the intervals when the heating current is suppressed. This end is achieved by means of a rotating commutator, which automatically establishes electric communication between the filament and the heating battery a certain number of times per second, and then after cutting off these connexions, replaces them by connexions between the filament, the anode, the high tension battery, and the apparatus for measuring the currents. If the commutator rotates sufficiently rapidly it may be assumed that the filament has not time to cool during the intervals when it is not heated, so that the experiments are carried out at a temperature as accurately known as in the classical arrangement. Schottky has been able to show that under these conditions saturation can be obtained with fields very much less than had been necessary previously, fields which are even practically zero if the electrodes are concentric cylinders.

In conclusion, it is apparent that the obstacles to saturation which we have just examined can be suppressed by suitable precautions. This is quite different from the case of the space charge, the existence of which is inherent in the phenomenon itself and the consequences of which are unavoidable.

4. The different parts of the saturation curve. To conclude this chapter we will examine, with Langmuir, the various parts of the saturation curve, taking into account only the essential causes which give rise to its form.

(*a*) Suppose that the tungsten filament which serves as the source of electrons is raised to such a temperature that

the saturation thermionic current is of the order of a milliampere. Keeping the temperature constant throughout the whole of the experiments, we will progressively increase the voltage on the anode and construct the curve which represents the current as a function of the potential difference between the anode and the filament, the volt-ampere characteristic.

So long as the potential of the anode is strongly negative with respect to that of the filament,* no electrons can reach it, and the current is zero. The current begins to assume measurable dimensions when the potential of the cylinder no longer differs from that of the filament by more than

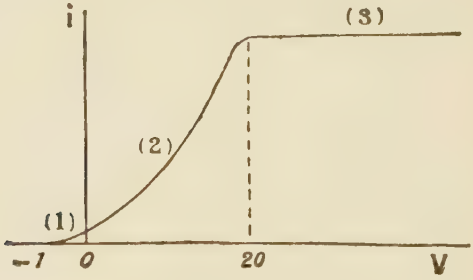

FIG. 12.

about one volt. In fact, it is at this moment that the initial velocities of some of the electrons emitted by the filament begin to be able to surmount the reverse field which opposes their motions and hinders them from reaching the cold electrode. This effect is accentuated as the potential of the anode approaches that of the filament (the latter is taken as zero), and the portion of the curve thus obtained (region 1) is of a form which follows immediately from Maxwell's distribution law. It is easy to see that this portion would be rectilinear if the logarithms of

* We assume that by some device, similar to that of the rotating commutator mentioned above, the filament is maintained at a constant potential during these measurements.

the currents were employed as *ordinates* instead of the currents themselves.

(*b*) Now suppose that the potential of the cylinder becomes positive. The current received by it will henceforward increase rapidly, since the field is in a sense favourable to the transfer of the electrons from the filament to the cylinder. But, as we are assuming that the saturation current can attain to a value of one milliampere, the total number of electrons emitted is sufficiently large to involve the mechanism of mutual repulsion which has been examined in detail above. The current will therefore increase proportionally to the 3/2 power of the applied voltage. The region 2 of the saturation curve is thus obtained, or the region corresponding to the phenomenon of the space charge. This second region must be distinguished from the first, and is governed by a totally different law. If it were desired to obtain a straight line for this region it would be necessary to use as *abscissae and ordinates* the logarithms of the variables V and i, instead of these variables themselves. In our particular case, with a saturation current of one milliampere, this portion of the curve will be prolonged up to an abscissa of the order of 20 volts.

(*c*) Finally, when the voltage on the anode is high enough, saturation will be attained ; this is the region 3 of the curve in which the current does not change whatever voltage be applied. This part of the curve is a horizontal line without any need to use logarithmic co-ordinates. The saturation current obtained can only vary if the temperature of the incandescent filament be changed at the same time ; the variation then follows Richardson's law. Thus we can consider the third portion of the curve as being governed by a new law, entirely independent of the two which have preceded it, namely, Richardson's law.

The three portions of the curve between which we have just distinguished and each of which corresponds to one of the properties of the electrons emitted (Maxwell's distribution law, the 3/2 power law, due to the space charge,

and Richardson's law), exist whatever the temperature of the filament, but they are developed to a greater or less extent according to the conditions of the experiments. For example, if a sufficiently low temperature is employed with the tube having cylindrical electrodes which we have considered hitherto, so that the saturation current does not exceed a few microamperes, the phenomenon of the space charge disappears almost entirely and the curve is reduced to the portions 1 and 3. The ascent of the curve occurs in the region of negative potential, at voltages only slightly different from zero (on account of the initial velocities), and saturation is attained very soon afterwards, commencing at voltages which are also practically zero. On the other hand, if the temperature of the filament is so high that the saturation current reaches several tens of milliamperes, the initial currents become comparatively so small that the region 1 vanishes almost completely. On the other hand, the region 2, which corresponds to the 3/2 power law, is more developed and may extend up to abscissae of 100 and even 200 volts. Saturation is then difficult, and the horizontal portion 3 will only be attained at very high anodic voltages. *Langmuir's Record* contains a large number of verifications of such forecasts which have been investigated to their most minute details.

CHAPTER VII

THE EFFECT OF GASES ON THE ELECTRONIC EMISSION

1. General remarks on the effect of gases. The presence of a gas in the tube in which the electronic emission is being examined often changes completely the aspect of the phenomena observed. If the pressure and the electric field are suitably adjusted the electrons emitted will be able to collide with the molecules of the gas and to acquire in the interval between two collisions sufficient energy to ionize these molecules. For this to occur the difference of potential which accelerates their motion during the interval between two collisions must exceed a certain critical value which varies with the gas and is called the *ionization potential* of the gas. If a large number of positive ions arise out of these collisions their motion in the field, which is in the opposite direction to that of the electrons, will be able to give rise to a large increase in the total current, especially if they acquire a kinetic energy sufficient for them, in their turn, to cause a supplementary ionization by collision. The circumstances are then favourable to the occurrence of a disruptive discharge.

These very well known phenomena which are manifested in all gases at relatively high pressures and in relatively intense fields, involve considerable increases in the saturation currents which are to be observed at a given temperature ; their examination is outside the scope of this book and will not be pursued further. Moreover, we will not persist in the examination of the question whether the electron loses its excess energy almost entirely when it encounters a neutral molecule (the case of a soft impact), or whether, on the contrary, it simply changes direction,

retaining wholly or in part its kinetic energy (the case of a completely or partially elastic impact). That is an extremely important problem which for many years has been the object of a large number of researches relating to resonance and ionization potentials. It will be sufficient for us to observe that the electronic current will satisfy laws expressing the variation with the applied voltage which can be predicted according to the hypothesis adopted concerning the nature of the collision with neutral molecules, and which differ appreciably in the two cases. For the detailed study of these questions reference should be made to papers and books specially devoted to them.*

We shall only investigate here the influence on the electronic emission from incandescent wires of a *very small* quantity of gas, the pressure of which will not in general exceed ten microns of mercury. Under these conditions it will still be possible for the phenomena associated with ionization by collision to be produced, but they will not become altogether preponderating. In particular, the complications arising from the nearness to disruptive discharge are avoided. As we shall see, even when the problem is restricted in this way the question of the influence of gases is still very complicated, and many of the difficulties have not yet been entirely solved.

2. Historical. The considerable influence of traces of gas on the electronic emission from incandescent substances was not known in the early stages of the work. Thus in the fundamental experiments of MacClelland, to which reference has been made above,† the thermionic currents were found to be independent of the pressure of the gas when this varied from 0·04 mm. of mercury down to the lower limit of 0·004 mm. It was concluded from this that, under the conditions of these experiments, the pressure

* In this connexion see, for example, Richardson, *Emission*, p. 79; L. Bloch, *Le Radium*, 1919, II, 358.

† Page 3.

of 0·04 mm. of mercury was sufficiently low for the electrons emitted by the filament no longer to encounter molecules of gas on their way to the anode. Ionization by collision thus being suppressed it was understood that the effect of the gas had itself vanished. Further, in the investigations for some time after this no special precautions were taken to push the vacuum to its farthest limits. Thus, in Richardson's experiments carried out with a view to examining the law of electronic emission as a function of the temperature, which led to the fundamental paper of 1903,* the pressure was simply permanently maintained below 0·001 mm. of mercury : it seemed that this vacuum should be sufficient to eliminate all complications due to the gas.

Difficulties commenced to appear with H. A. Wilson's work on the emission from platinum in various gases, a research which was slightly later than that of Richardson.† This author found that the electronic currents obtained from platinum in a very rarefied gas were nearly independent of the nature of the gas in the case of air, nitrogen, or water vapour. On the other hand, the emission was enormously increased by traces of hydrogen. Wilson was thus led to attribute to the occluded hydrogen a preponderating influence in the thermionic emission from platinum. He sought, therefore, to reduce this emission by reducing the quantity of hydrogen. In some experiments, before the platinum wire was heated in a vacuum it was subjected to the prolonged action of oxidizing agents ; for example, it was heated for many hours in nitric acid. The thermionic emission was reduced in striking proportions ; in one of the trials it became 250,000 times less than before. These experiments were repeated by Richardson and gave rise to numerous discussions some of the results of which will be given later.

The fact that hydrogen has a considerable influence on the thermionic emission of platinum furnishes a very

* Richardson, *Phil. Trans.*, 1903, 201, 497.
† H. A. Wilson, *Phil. Trans.*, 1903, 202, 262.

important argument in favour of the chemical theory of the phenomenon. Indeed, it might be thought that in spite of the impossibility of entirely reducing the emission to zero, even after very prolonged oxidizing treatment, the residual emission was none the less due to the last traces of hydrogen, and that ultimately the emission from platinum in a perfect vacuum would be nil. This point of view was still further justified by some experiments carried out on the alkali metals and on heated salts. It needed the employment of refractory metals such as tungsten and molybdenum, combined with more perfect vacuum technique, to show that it was essential to return to the intrinsic theory, and that the complicated case of platinum was a relatively isolated one. We shall return to this case later. For the time being we will abandon the chronological order and begin to examine the influence of gases by means of the case which would seem to present the simplest aspect, namely, that of tungsten in a very rarefied atmosphere of a gas nearly inert from the chemical point of view.

3. Tungsten in an inert gas under very reduced pressure. We shall suppose that the tungsten filament to be used as the source of electrons has been placed in a tube provided with another electrode and that a perfect vacuum has first been produced in the tube, all the precautions mentioned in Chapter II having been taken. The apparatus having been prepared in this way, a trace of one of the following gases is introduced into the tube : argon, mercury vapour or hydrogen. The pressure must not exceed a few thousandths of a millimetre of mercury. The first two gases can be considered as completely inert from the chemical point of view with respect to tungsten. The third can give rise, as we shall see later, to certain reactions, but, actually it behaves in nearly the same way as the others.

In the very simple case which we have postulated, it is

easy to indicate the way in which the thermionic currents are modified by the presence of the gas. We shall give the result in the form in which it has been stated by Langmuir as the result of a very large number of experiments. To this end let us refer to the saturation curve which can be constructed at a given temperature in a perfect vacuum, the various characteristics of which have been examined in the previous chapter. This curve is reproduced in Fig. 13, and on the same diagram the deformation of one part of the curve by the presence of the gas is shown by the dotted curve.

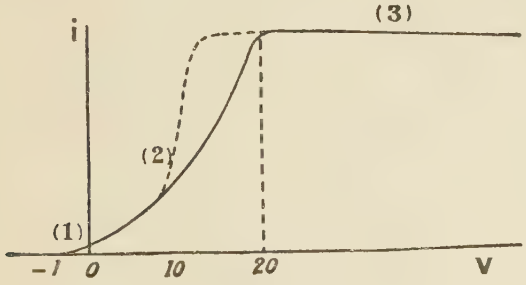

FIG. 13.

It is seen that the first part of the curve (region 1), which corresponds to the existence of initial electronic velocities distributed according to Maxwell's law, is not modified at all. The same is true of region 2, corresponding to the presence of a space charge and to the 3/2 power law, as far as a certain critical voltage, which is about 10 volts in the figure. From this point it is seen that the 3/2 power law is no longer satisfied; the current increases *more rapidly* than it should do according to the law, and it may even increase so rapidly that the curve ascends almost vertically, as in the figure. Finally, for an applied voltage a little greater than that mentioned, saturation is again attained: the current becomes constant with the *same value* as is reached in a perfect vacuum.

These results are remarkable from several points of view, although their interpretation as given by Langmuir does not appear to present any great difficulty. No modification of the curve occurs before a definite critical potential is reached because at low voltages the electrons do not acquire during their passage through the gas sufficient kinetic energy to provoke ionization by collision. The critical potential at which the curve rises abruptly is the ionization potential of the gas. In the case where the rise is sufficiently sharp the abscissa which corresponds to it can be ascertained with reasonable accuracy. This experiment thus yields a method of determining ionization potentials which has been employed in particular by Foote,* and which gives results in good agreement with those obtained by other methods.

When the ionization potential of the gas has been reached the electrons, which encounter several molecules of the gas in spite of the rarefaction of the gas, commence to give rise to ionization by collision, and this causes the appearance of a certain number of positive ions. These positive ions begin to move towards the incandescent filament which acts as the cathode but as their mass is very much greater than that of the electrons this movement will be relatively slow, so that, even assuming that their charge has not been neutralized *en route* by another electron, they will only carry through the gas an insignificant supplementary current. An important alteration of the current cannot therefore be expected on account of the feeble ionization by collision which takes place in the rarefied gas. This prediction is completely confirmed by the examination of the portion of the curve which corresponds to saturation, the saturation current being the same as if all gas were entirely absent. On the contrary, it is in apparent disagreement with the dotted portion of the curve, the ordinates of which are much larger than those of the corresponding curve obtained in a vacuum. This

* Foote, *Phys. Rev.*, 1919, 13, 64.

is because the mechanism of the increase of current is in this case an *indirect* consequence of ionization by collision. The positive ions though few in number remain in the gas for a relatively long time since their inertia is very great. They are able therefore to create a positive space charge which, in spite of the small number of these ions, becomes comparable with the negative space charge arising from the electrons. As soon as the negative space charge is to a large extent neutralized the effect of the mutual repulsion between the electrons, which opposes saturation, disappears and the region 2 of the old saturation curve also tends to vanish as it was due to this cause. Thus the abrupt rise of the curve as soon as ionization by collision sets in is easily explained. It is not the number of electrons emitted which is increased but only the number of electrons which are able to arrive at the anode.

It is possible to support the preceding argument with figures in such a way as to render it even more plausible. Suppose that the gas examined is mercury vapour at a pressure of one-tenth of a micron. The two electrodes are assumed to be one centimetre apart; the mean free path of an electron at the pressure postulated is of the order of 600 centimetres. On the average, therefore, one out of every six hundred electrons will encounter a mercury molecule in the passage from one electrode to the other. If each collision with a molecule is followed by ionization, which will be the case if the electric field is large enough, the number of positive ions produced will be 1/600 of the number of electrons. If, further, the mobility of the positive ions is, for example, 1/600 of that of the electrons, the current carried by the former will only be 1/360000 of the original current; it will thus be entirely negligible. On the other hand, the space charge created by these particles, six hundred times less numerous but six hundred times slower than the electrons, will be of the same order as the negative space charge, so that on the whole the space charge will become approximately nil, and the current

curve will rise much more abruptly than when this cancellation does not occur.

A final conclusion to be drawn from these results is as follows. The presence of a trace of an inert gas in a thermionic emission tube can only be revealed by a careful and complete examination of the saturation curve. Formerly it was believed, and this opinion is still maintained in some recent papers, that the presence of a trace of gas was always made manifest by an increase in the saturation current because of ionization by collision. This view, which is certainly justified in the case of pressures high enough for the number of ions produced by collision to be comparable with the original number of electrons, is no longer true at low pressures. Langmuir has published an account of some tubes into which a trace of mercury vapour was introduced sufficient for the electric discharge to become visible under the form of a blue glow, but which nevertheless furnished a saturation current equal to that obtained before the introduction of the vapour. In order to disclose the existence of the trace of gas introduced it is necessary to draw the current-applied voltage curve in the region between saturation and the ionization potential.

4. Tungsten in a chemically active gas. When a trace of a gas such as oxygen, nitrogen, or water vapour, capable of acting chemically on tungsten, is introduced into the tube with a tungsten filament, the thermionic phenomena become much more complex; new characteristics which result from the chemical changes are superposed on the preceding effects. For example, if the active gas can unite with the tungsten to form a compound which is not too volatile at the temperature of the filament, this compound will be formed on the surface of the filament, and the chemical change will involve, as in the case of Wehnelt cathodes, an alteration in the thermionic emission. In this connexion two types

of modification can be expected *a priori* : if the compound formed is more active than tungsten the thermionic emission will be increased, and on the contrary it will be diminished if the reverse is true.

As a matter of fact the compound WO_3 which oxygen forms with tungsten has long been known. This same compound can be formed when water vapour is reduced by tungsten. On the other hand Langmuir has discovered, in the course of his researches on tungsten filaments, compounds of tungsten with hydrogen and nitrogen the chemical formulae of which are very probably WH_2 and WN_2. A modification of the thermionic emission is to be expected, therefore, with all the gases mentioned. In fact, this modification does occur, and it is very remarkable that in no case so far has an *increase* of emission been established. For all the chemically active gases the thermionic emission is less than that in a vacuum. It should be remembered that for the chemically inert gases examined above, the thermionic emission remained the same as in a vacuum. Further, it must be understood that it is the saturation current which is referred to in both cases, for below saturation we have seen that it is possible to observe, even with inert gases, apparent increases in the current due to the partial neutralization of the space charge.

The fact that in any rarefied gas whatsoever the electronic emission from tungsten is never greater than in a perfect vacuum is a very strong argument in favour of the intrinsic theory of emission. In fact it is difficult to conceive that an emission due to chemical reactions between the metal and the residual gas should attain its maximum value when the vacuum is made as perfect as possible, i.e. when all cause of reaction is suppressed with the greatest care.

A second important fact which is observed with chemically active gases, to which hydrogen must be added in this case, is their progressive and spontaneous disappearance from the tube containing the heated tungsten

filament.* This spontaneous 'cleaning up' of the tube produces a corresponding improvement in the vacuum which may ultimately become as good as before the introduction of the trace of gas. It is clear that this phenomenon is a consequence of the formation of some new chemical compounds at the expense of the gas introduced or of the tungsten, compounds which are deposited on the filament or absorbed by the walls of the tube. We shall later resume the consideration of some of these compounds

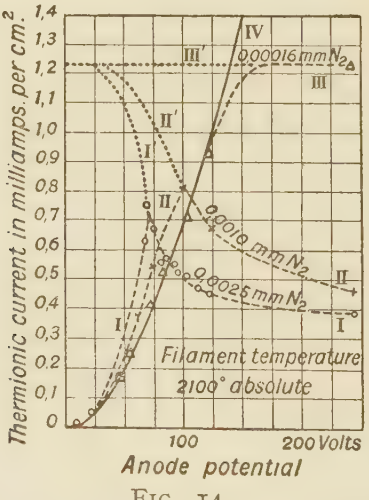

FIG. 14

the study of which has led Langmuir to a whole series of chemical conclusions of great interest.

For the time being it will be sufficient to give as an illustration the complications which result from the presence of a trace of nitrogen in a thermionic tube having a tungsten filament. The curves which summarize the facts are shown in Fig. 14, and are taken from a paper by Langmuir.†

* This is what Langmuir has called the 'cleaning up effect.'

† Langmuir, *Phys. Rev.*, 1913, 2, 450.

The experiments were all carried out at a temperature of 2,100 degrees absolute. The applied voltages are used as abscissae and the currents as ordinates; the curves drawn are therefore saturation curves. The continuous curve represents the 3/2 power law to which theoretically the middle portion of the curves should conform. The broken curves are the experimental curves obtained with pressures of nitrogen which are respectively 0·0025 mm. (curve I), 0·0010 mm. (curve II), and 0·00016 mm. (curve III). Curve III, which corresponds to a very low pressure of nitrogen, less than two-tenths of a micron of mercury, has approximately the same shape as if the vacuum had been perfect. It is composed of the three classical regions: the presence of the gas at this very low pressure is not manifested by any visible result. On the contrary, the two other curves are very different. At first they rise more rapidly than the theoretical curve, but at a certain voltage, different for each of them, they re-descend rapidly and tend towards a limiting value of the current. The initial rapid ascent of these two curves is easily explained by the considerations already developed for inert gases: it is due to the ionization by collision causing the appearance of positive ions the charge of which neutralizes the negative space charge due to the electrons and this gives rise to a divergence from the 3/2 power law. The chemical effects only manifest themselves in the descending portions of these two curves. When the voltage applied to the anode is sufficiently great the positive ions, produced by collision and moving towards the filament, will reach it in sufficiently large numbers to combine with the atoms of tungsten (probably with the atoms of tungsten vapour emitted by the filament) and form a nitride capable of being deposited on the filament. The greater the voltage the more favourable are the conditions to the formation of this nitride. Thus the filament will be covered to an increasing extent by the new compound and the thermionic emission will tend progressively towards that which

corresponds to this compound. The curves I′ and II″ in the figure represent the increasing rate of production of the tungsten nitride at the surface of the filament, and combine with the old saturation curves to give the experimental curves I and II.

5. Platinum in hydrogen. We will now return to the thermionic emission of platinum in a rarefied atmosphere of hydrogen. This case which was one of the first investigated is also one of the most complicated and has given rise to numerous controversies.

We know already that platinum in the presence of a trace of hydrogen behaves in a manner opposite to tungsten. That is to say, the thermionic current is much greater in the presence of the gas than in a perfect vacuum. H. A. Wilson,* and subsequently Richardson,† have carried out numerous experiments on this question, the results of which are partially contradictory. The facts most firmly established are as follow.

In the first place, Richardson's law is satisfied in all cases, but the constants a and b of the formula depend on the pressure of the hydrogen and on various other experimental conditions. In the first experiments of H. A. Wilson, which were made with *new* filaments, that is to say, with filaments which had not been subjected to prolonged heating in hydrogen before the measurements were made, the saturation current at constant temperature could be represented very accurately by a formula of the type

$$i = Ap^z, \quad \ldots\ldots\ldots\ldots\ldots\ldots (27)$$

where p represents the pressure of the rarefied gas, and A and z are constants independent of the pressure but depending on the temperature. The constant z was

* H. A. Wilson, *Phil. Trans.*, 1903, 202, 263 ; *ibid.*, 1908, 208, 247 ; *Proc. Roy. Soc.*, 1909, 82, 71 ; *Electrical Properties of Flames*, London, 1912, p. 16.

† Richardson, *Phil. Trans.*, 1906, 207, 1.

always between 0·5 and 1. When the temperature was changed the values of the constants changed, but it took a long time to arrive at a new permanent regime: it is probable that it is the hydrogen dissolved in the platinum which plays the most important part in the phenomenon and that this hydrogen is somewhat slow in attaining equilibrium with the metal and the remaining gas.

A very different state of affairs is observed when the experiments are carried out with an *old* filament, which has been heated in hydrogen for a long time. It is then found that the emission is practically independent of the pressure when this is between one millimetre and 0·001 mm. of mercury. It is even possible for a filament which has been saturated with hydrogen at a relatively high temperature and pressure to liberate fairly considerable qualities of hydrogen when the pressure is lowered, without its thermionic emission being appreciably altered.

The explanation of these characteristics is to be found in the following hypotheses: A new filament only contains dissolved hydrogen; on the contrary, an old filament may have combined with the hydrogen to some extent, the combination taking place, however, at an extremely slow rate. At a given temperature there would be a tendency to the establishment of equilibrium between the four phases platinum, platinum hydride, solution of hydrogen in platinum,* and gaseous hydrogen. The dissociation pressure of the hydride at the temperatures attained in the experiments (under 1,400 degrees) must be very small (less than 1/1000 of a mm. of mercury) since the activity of an old platinum filament cannot be eliminated entirely by prolonged heating in a vacuum. It must also increase fairly rapidly with temperature since the activity of an old filament can be destroyed almost instantaneously by heating in an atmosphere of oxygen. These considerations account for a fairly large number of

* It is even possible that some of this dissolved hydrogen is dissociated into ions.

facts, particularly for the very definite difference which exists between new and old filaments.

Nevertheless, they are far from being sufficient if the study of the phenomena is pursued to the smallest details. Richardson and H. A. Wilson have observed certain anomalies in the variations of the currents with the applied voltages and with the time; a detailed account of these will be fo und intheir papers and their interpretation remains open to considerable doubt. The question deserves re-examination.

We will not devote much time to the theoretical attempts which have been made by Richardson to explain the variation of emission with pressure. It need only be noticed that the empirical formula (27) proposed by H. A. Wilson cannot be suitable for all pressures since it leads to a zero current in a perfect vacuum, whereas the current should be reduced to a limiting value different from zero. It is conceivable that this formula might be replaced by one of the type

$$i = A(1 + ap^b)^z, \quad \ldots\ldots\ldots\ldots (28)$$

the parameters A, a, b, and z being so chosen that formula (28) becomes identical with Richardson's formula at a given pressure.

There is another important observation to be made relative to the effect of gases on the thermionic emission. Every variation of this emission is connected as we have seen, with a variation of the contact potential difference between the metal investigated and a typical metal (such as platinum in a vacuum) taken as a standard for comparison. For example, platinum in a vacuum and platinum in hydrogen must exhibit at a given temperature a contact difference of potential which is a function of the pressure of the hydrogen.

In a fairly recent paper Richardson and Robertson*

* Richardson and Robertson, *Phil. Mag.*, 1922, 43, 162.

have attacked this question for platinum and tungsten in hydrogen, seeking to demonstrate the variations of the potential difference by thermionic methods. To this end they constructed the curves giving the thermionic current as a function of the applied voltage at a given temperature, limiting themselves to very low voltages, i.e. to the beginning of the saturation curve. They found that this curve was displaced parallel to the axis of abscissae without appreciable deformation when a small quantity of hydrogen was introduced into the tube. It is natural to consider this shift of the curve as representing the change in the contact potential difference between the metal and the gaseous medium. Moreover, the order of magnitude of the displacements observed is in good agreement with the variations which can be predicted from the theoretical considerations mentioned above.

When the theories connecting thermionic phenomena with the contact differences of potential and with thermoelectric phenomena have been developed on a really sound basis experiments of this type are certain to throw considerable light on the mechanism of the phenomena.

The researches which have been carried out on the influence of gases on the thermionic emission from *metallic oxides* can also be considered at this point. The influence of hydrogen on the emission from Wehnelt cathodes has been investigated by Horton * and Martyn † both of whom observed, as in the case of platinum, considerable increases in the emission, at least when the pressure of the hydrogen was sufficiently high. There is no doubt that the chemical action of the hydrogen ions is involved in this case. Other gases also have the power of modifying the emission from Wehnelt cathodes: Fredenhagen ‡ and J. J. Thomson § have given several examples of this, but here again the

* Horton, *Phil. Trans.*, 1907, 149, 207; *Proc. Roy. Soc.*, 1915, 91, 322.

† Martyn, *Phil. Mag.*, 1907, 14, 306.

‡ Fredenhagen, *Phys. Zeits.*, 1914, 15, 19.

§ J. J. Thomson, *Conduction of Electricity through Gases*, p. 478.

interpretation which is to be placed on the results obtained remains in doubt and the way lies open to further research. In the same group of investigations may be included the experiments of Lilienfeld * who has obtained some rather conflicting results in which traces of gas probably play a somewhat important part.

6. Chemical phenomena at very low pressures. This chapter, which has been devoted to the consideration of the influence of rarefied gases on the thermionic emission, will be concluded with a few remarks on the researches of a chemical nature which have been undertaken in connexion with this emission, and which have led Langmuir † and his collaborators to several very remarkable results.

When a rarefied gas is introduced into an evacuated tube containing an incandescent tungsten filament and a cold electrode raised to a higher potential, the molecules of the gas may undergo chemical changes in contact with the filament, and the products of the reaction may be prevented by the electric field and by the rarefaction of the gas itself from behaving in the ordinary manner. Under these conditions certain chemical reactions are found to occur which are quite different from those which would take place if the gas molecules could collide frequently as at higher pressures, instead of being projected towards the walls of the tube where they are often absorbed. Only a few examples of such anomalies will be given, our object being simply to show that advances in chemistry itself may be attained by researches which, at first sight, appear to be entirely foreign to this branch of science.

In the first place, we have already seen that if a trace of nitrogen is introduced into an evacuated tube provided with a tungsten filament a progressive diminution of the

* Lilienfeld, *Ann. der Phys.*, 1910, 32, 675 ; 1914, 43, 24.

† Langmuir, *Jour. Amer. Chem. Soc.*, 1912, 34, 860 ; 1915, 37, 417 and 1139.

nitrogen is observed. At the same time the tungsten filament decreases in weight, but this decrease is quantitatively the same as occurs in a vacuum. The conclusion to be drawn from this is that the tungsten and the nitrogen do combine but that the combination can only take place between the molecules of nitrogen and those of the tungsten vapour emitted by the filament: each of these latter molecules as it is evaporated will combine with nitrogen. The chemical formula of the compound produced results from a comparison of the velocity of disappearance of the gas with the velocity of evaporation of the tungsten; it corresponds to the formula WN_2. Some of this compound may be deposited on the filament, and the electron emitting power of the latter thus diminished (see page 81), but it may also be deposited on the walls of the tube itself. In this case it forms a brown deposit easily distinguishable from the black deposit of metallic tungsten. If the tube be opened and moist air introduced a strong smell of ammonia is perceptible.

These experiments have been completed by the investigation of the chemical reactions which can be obtained with oxygen, hydrogen, the compounds of carbon and oxygen, and so on. In the majority of cases it becomes necessary to develop a method of quantitative analysis by means of which the composition of a few cubic millimetres of a mixture of several of the common gases mentioned above can be examined. Langmuir has been able to carry out this work successfully and to accomplish these analyses correct to within two or three per cent by the use of what is really a eudiometric method.

If hydrogen is used in a tube with a filament of tungsten, platinum or palladium heated above 1,300 degrees absolute, some of the molecules of hydrogen which strike the filament are dissociated into atoms. This atomic hydrogen, the formation of which has been verified by accurate measurements of the heat of dissociation up to temperatures of the order of 3,000 degrees, has very curious properties. It is

very easily absorbed by the walls of the tube, particularly by those regions which are very cold. If a portion of the wall be cooled with liquid air it absorbs relatively considerable quantities of atomic hydrogen. On the other hand, as this hydrogen has a chemical activity very much greater than molecular hydrogen unforeseen consequences may result. For example, if a trace of hydrogen is introduced into a previously evacuated tube and time allowed to elapse till the hydrogen has practically disappeared by reason of its progressive dissociation into atoms, and the absorption of these atoms by those portions of the walls of the tube which are cooled by liquid air, it is found that on removal of the liquid air there is a liberation of gas which cannot be recondensed by a second application of the liquid air. In fact, the atomic hydrogen liberated when the liquid air was removed has changed, by combination of its atoms, into molecular hydrogen, on which a cold wall has no action. In this experiment, if a little oxygen is introduced into the tube after the initial disappearance of the hydrogen, it is frequently found when an analysis of the gases in the tube is made immediately afterwards, that no trace of oxygen but only of hydrogen remains. This paradoxical result is explained by assuming that the molecules of oxygen have combined with the active atoms of hydrogen adsorbed by the walls of the tube to form molecules of water vapour and that these have remained in contact with the walls. At the same time the collisions of the molecules of oxygen against the cold walls surcharged with atoms of active hydrogen have given rise to the liberation of a certain number of these atoms which have re-combined in pairs to regenerate molecules of hydrogen.

Some very striking experiments have also been carried out with chlorine. If a tungsten filament is heated momentarily in a well evacuated tube to a temperature of 3,000 degrees absolute it partially volatalizes and forms a black deposit of metallic tungsten on the walls of the

tube. If a trace of chlorine is now introduced into the tube in the cold it does not appreciably attack either the filament or the deposit, even though the tube be heated to 200 degrees. But if the filament be raised to a bright red heat, keeping the tube cold, the deposit of tungsten *on the tube* is seen to disappear rapidly without the heated filament suffering any visible alteration. It is probable that the molecules of chlorine have been dissociated into active atoms by their collisions with the heated filament and that the atoms thus produced, projected in straight lines towards the walls without being able to recombine *en route* with other similar atoms, unite there with the tungsten at ordinary temperature.

The experiment is still more striking when two filaments which can be heated independently are placed in the same evacuated tube. If a trace of chlorine, which has no action on tungsten in the cold, be again introduced and one filament is heated, it is found that it is only the *other* filament, kept at the ordinary temperature, which disappears gradually under the action of the chlorine.

We shall not extend this list of examples, several of which have been quantitatively verified, and which appear to be sufficient to show the very great interest presented by such investigations. It is conceivable that these researches are closely allied with those relating to the adsorption of gas by solid surfaces. In fact Langmuir has developed a very interesting theory of adsorption in which he makes monomolecular layers play an essential role, but reference should be made to the original papers for the study of this question.

CHAPTER VIII

THE EMISSION OF POSITIVE IONS BY METALS IN A VACUUM AND IN GASES

THE emission of positive ions by incandescent bodies was discovered and investigated at the same time as the emission of negative charges. We have already mentioned (Chapter I) the early experiments of Guthrie according to which an iron ball heated to dull red in air can retain a negative charge but not a positive one. Elster and Geitel (see the bibliography in Chapter I) were the first to show that *new* metallic filaments heated for the first time in a vacuum or in various gases emit only positive ions at moderate temperatures. The emission of negative ions commences at higher temperatures and this may mask completely the positive emission. The latter is due to ions of atomic dimensions. Like the negative emission it seems to be due to the metal itself and not to the action of the surrounding gas. Its investigation is rendered difficult by various circumstances, the principal of which are indicated below. As it has not received practical applications of importance comparable with those of electronic emission it will be sufficient for us to indicate the more firmly established facts, referring the reader to the original papers or to Richardson's book for details.

1. The influence of the time of heating. The first point to be noticed in the study of the positive emission in a vacuum is its *decrease with the time*. The decrease is the more rapid the higher the temperature and in some cases presents rather complex characteristics. To give an idea of

these, two curves taken from Richardson's papers * are reproduced in Fig. 15 ; they show, for a given temperature the law of variation of the current as a function of the time. For the first curve the decrease is approximately exponential ; in the second, an initial rapid decrease followed by a slight recovery and again by a final fall is to be observed. These curves immediately recall some of the curves showing the activity of radioactive substances. In the first case it is as if the heated wire were covered with a substance capable of emitting positive ions (the active substance)

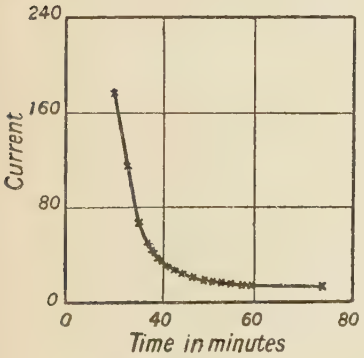

FIG. 15

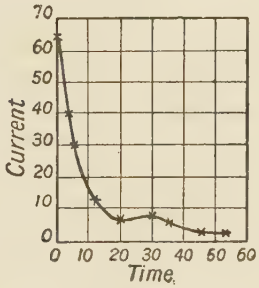

FIG. 15A

which decomposed or evaporated in the course of time according to the law of radioactive transformations, i.e. with a velocity proportional to the quantity of substance present. In the second case, the active substance in disappearing gives rise to a second, inactive, substance which decomposes in its turn, producing a third, active, substance.

Whatever the correct interpretation to be given to

* Richardson, *Phil. Mag.*, 1903, 6, 80 ; *C. R. du Congrès de Radiologie de Liège*, 1905, p. 50. See also Sheard, *Phil. Mag.*, 1914, 28, 170.

these facts, it is evident that such variations completely differentiate the emission of positive ions from the negative emission previously examined, which is manifested as a perfectly constant phenomenon. They cannot occur without rendering the experiments much more difficult than those hitherto described.

2. Saturation curves. In particular, it is necessary to take into account the variations of the emission with time when it is proposed to draw the saturation curve at a given temperature. Such a curve can only be drawn correctly if the experiment is conducted at a temperature so low that the variation of the emission with time is greatly reduced. The disadvantage in working at low temperatures is that the currents observed are very weak and this necessitates the employment of sensitive electrometers as measuring instruments.

With these precautions it is possible to draw a curve giving the variation of the current with the applied voltage. In general this curve presents complications which are difficult to explain. Thus Richardson and his collaborators * have frequently observed with platinum currents increasing from 0 to about 5 volts ; between 5 and 40 volts the current remains constant or *decreases* slightly ; and finally, between 40 and 400 volts the current increases approximately proportionally to the voltage, but this increase, which is very definite with new platinum wires, slowly disappears in course of time. It may reappear if the temperature is raised or if air is admitted into the apparatus. Further experiments are necessary to explain these characteristics.

3. The regeneration of old filaments. When a wire has been subjected to prolonged heating in a vacuum so

* Richardson, *Phil. Mag.*, 1903, 6, 80 ; *Phil. Trans.*, 1906, 207, 11. Richardson and Sheard, *Phys. Rev.*, 1912, 34, 391 ; *Phil. Mag.*, 1916, 31, 497. Lester, *Phil. Mag.*, 1916, 31, 549.

that its positive emission which decreases with the time to a very considerable extent, has fallen nearly to zero, it is possible temporarily to regenerate the faculty of emission by a very large number of methods. The principal of these are as follow:

1. A new filament is placed near to the one to be regenerated, and momentarily heated. The active substance then distils from the new wire to the old and the latter again becomes capable of emitting ions for a certain time.

2. The exhausted wire can be placed in a luminous discharge at low pressure, in the neighbourhood of the cathode, or may itself be used as the cathode. There is no doubt that the bombardment of the wire by the moving particles in the tube plays an important part in the regeneration. The phenomenon is much less marked in hydrogen than in air, nitrogen, or oxygen.

3. It is sufficient merely to heat the tube which contains the filament.

4. The filament may be subjected to the action of a gas under high pressure.

5. It may be subjected to mechanical actions, etc.

4. The variation with temperature. The difficulty of obtaining a saturation current, together with the decrease of the emission with time, makes the investigation of the law of the variation of the positive emission with the temperature rather a hard problem. Nevertheless, this work has been carried out by Strutt * with copper, silver. and copper oxide; by Wehnelt † with the oxides of the alkaline earths; and by Owen ‡ with the filaments of Nernst lamps. Richardson's law is satisfied in all cases: the constant b which occurs in the exponential term is

* Strutt, *Phil. Mag.*, 1902, 4, 98. See also Richardson, *B. A. Reports*, Cambridge, 1904, p. 473.

† Wehnelt, *Ann. der Phys.*, 1904, 14, 425.

‡ Owen, *Phil. Mag.*, 1904, 8, 249.

very much less (four or five times) than that which is found in the formula relating to the electronic emission of the same substance. This result is in agreement with the observation already mentioned that the positive emission increases much less rapidly with the temperature than the electronic emission.

Richardson * and Brown † have studied the law of distribution of the velocities of positive ions using the same experimental methods as for the negative electrons. They have examined a large number of substances and in each case they have deduced from their measurements a value of the perfect gas constant by the methods described above. All the values obtained are of the same order of magnitude as the theoretical number so that there is no reason to doubt that the positive ions, like the electrons, have their velocities distributed according to Maxwell's law.

5. The nature of the ions emitted. By far the most interesting question which arises in connexion with the positive emission from metals in a vacuum is to know what is the nature of the ions emitted. The best way of answering this question is to measure the ratio e/μ of the charge to the mass of the positive particle, as with the electrons. On the other hand, if e/m is used to denote the corresponding ratio for the hydrogen ion in electrolysis, the numerical value of which is known to be 9650 electromagnetic units, and if the second ratio is divided by the first, a quotient M will be obtained which can be called the electric atomic mass of the ion investigated. If this ion is composed of an atom carrying a single elementary charge, the number M must be identical with the ordinary atomic mass. If the charge is double the elementary charge (the case of a divalent ion), the electric atomic mass is then only half the ordinary atomic mass, and so on.

* Richardson, *Phil. Mag.*, 1908, 16, 890.
† Brown, *Phil. Mag.*, 1909, 17, 355 ; 1909, 18, 649.

The first experiments were carried out by J. J. Thomson* using the cycloid method, which employs crossed electric and magnetic fields and which has been described in connexion with electronic emission on page 4. The metal examined was platinum heated in air for a fairly long period under a pressure of 0·007 mm. of mercury. The values of M varied between 161 and 13·4, the latter number being obtained for the majority of the ions. If the carriers of the charge had been platinum atoms having one elementary charge, the value obtained should have been equal to the atomic weight of platinum, which is 192. On the other hand, if the atoms of the constituents of air were concerned (N = 14 and O = 16), the number should have been of the order of 14 or 16. In fact, it is not impossible that in these experiments the conductivity must be attributed to the ions taken from the surrounding medium.

The question has been re-examined in detail by Richardson † who has examined not only filaments which have

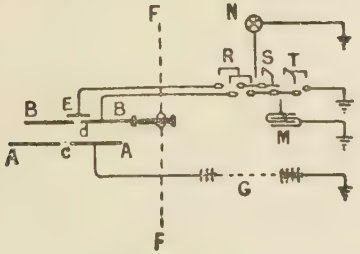

FIG. 16

been heated in a gas for a long time but also new filaments. In addition, he has endeavoured to increase the accuracy of the measurements. The apparatus used in the first place is very similar to that which was employed to study

* J. J. Thomson, *Conduction of electricity through gases*, 1912, p. 218.

† Richardson, *Phil. Mag.*, 1908, 16, 740; *Proc. Roy. Soc.*, 1914, 89, 507.

the distribution of the tangential components of the velocities in the emission of electrons (see page 45) ; it is represented diagramatically in Fig. 16. In an evacuated tube the heated metallic strip *c* in the same plane as the electrode A, sends positive ions towards the slit *d* which is cut in the plate B parallel to A. The electrode placed behind this slit and connected to a sensitive electrometer, receives those of the positive ions which have passed through the slit. Connexion with the electrometer can also be made in such a way that it is possible to ascertain the total quantity of electricity received by the plate B. Finally, the displacement of the whole of the upper system by means of a micrometer screw permits the collection of the ions emitted by the strip in various directions. A uniform magnetic field of suitable intensity can be established perpendicular to the plane of the figure.

The apparatus can be used in several ways. If the connexions are made as in the figure, the keys R and T are first pressed, which brings the electrometer to zero. Then if the key T is raised the electrometer will receive through the electrode E the charge which has passed through the slit *d*, whilst the condenser M will collect the charge received by the plate B. The key R is next raised and S closed ; then the electrometer measures the charge accumulated in the condenser. The comparison of the two deflections enables the charges which have passed through the slit to be compared with those which have been stopped by the whole of the plate B. By progressively displacing the slit *d* it is possible to ascertain the distribution of the charges emitted in various directions in known electric and magnetic fields. The curve obtained not only allows the accurate calculation of the ratio e/μ of the charge to the mass of the particles emitted, but also enables us to form an idea of their homogeneity. If they are not sufficiently homogeneous, if a mixture of two types of ions is concerned, for example, the curve obtained will present two distinct maxima from each of which a ratio

e/μ for the corresponding ions can be calculated. As a matter of fact the homogeneity of the ions emitted is fairly satisfactory and it has proved to be possible to use the apparatus with a simplified technique which allows an immediate comparison between the electric atomic masses of the ions emitted under various conditions.

In the first series of experiments* the following table was obtained :

Substance	Value of M (O=16)
Platinum	26·8
Palladium	30·5
Copper	28·3
Silver	30·0
Nickel	27·1
Osmium	24·5
Gold	47 to 23·1
Tantalum	13·3 to 21·1
Tungsten	42·1
Brass	28·8
Steel	30·0
Nichrome	24·5
Carbon	29·1

These figures cannot pretend to any great accuracy on account of the lack of uniformity of the electric field and the bending of the heated metal strip due to its expansion. The numbers obtained are probably too small. It will be noticed that with the exception of those relating to tungsten and those obtained at the beginning of the heating with gold and tantalum, all the numbers are comprised between 21·1 and 30·5, with a mean value of 26·9. These results, in spite of their imperfection, are interesting in that they show that the ions are not definitely derived from the heated substance, in the general case at any rate. In fact the atomic weights of the substances used lie between

* Richardson and Hulbert, *Phil. Mag.*, 1910, 20, 545.

192 (platinum) and 12 (carbon). The intervention of some impurity common to all the substances examined is therefore probable, but in order to elucidate this question it is necessary to have recourse to other and more accurate measurements.

These measurements have been made by Richardson, the apparatus having been improved.* The metal strips under examination were held taut by springs, which limited the number of substances which could be employed. Precautions were also taken to ensure the uniformity of the electric and magnetic fields. Finally, the measurements were made by comparison with the positive ions emitted by potassium sulphate, the homogeneity of which

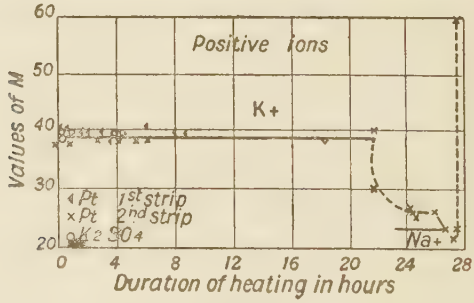

FIG. 17

had been recognized previously, and which consist of atoms of potassium carrying a single elementary charge.

The results of a typical experiment made with two strips of platinum are shown in Fig. 17. The times during which the metal had been heated, measured from the beginning of the experiments, are plotted as abscissae, and the values of the electric atomic mass M of the ion emitted are used as ordinates. It can be seen that during the first twenty hours the ions emitted had an atomic mass near to 39, indistinguishable from that of the potassium

*Richardson, *Proc. Roy. Soc.*, 1914, 89, 507.

ions emitted by the sulphate. After 20 hours the electric atomic mass fell fairly rapidly to the neighbourhood of 23, a value near to that which would correspond to sodium ions. It again ascended towards the end, a little before the rupture of the platinum strip, to about 60, which might be considered to be due to iron ions ($Fe = 56$).

The whole of the results are collected in the following table:

Substance	Duration of the Measurements	No. of Measurements	Extreme Values of M	Mean Value of M
Platinum, not specially cleaned	5 hrs.	16	39·75 to 45·2	40·0
Platinum, cleaned with acids, etc.	520 min.	33	39·1 to 41·6	40·1
Platinum, cleaned with acids, etc.	36 hrs.	—	38 to 40·1	39·1
Potassium sulphate	280 min.	10	39·2 to 41·1	40·2
Manganin, cleaned	4 hrs.	13	39·3 to 41·4	40·0
Iron, cleaned	55 min.	4	39·8 to 40·0	39·9
Iron, cleaned	315 min.	11	38·3 to 42·1	40·1
Platinum, regenerated by heating in air	160 min.	11	37·9 to 39·8	39·0
Platinum, regenerated by heating in a bunsen	133 min.	11	39·0 to 40·7	40·0
Manganin, regenerated by mechanical action	—	—	——	39·4

These figures relate to the initial emissions from the various substances mentioned. It will be noticed that all the electric atomic masses obtained are remarkably concordant so that the number of substances which can be regarded as characterizing the chemical nature of the

ions emitted is very small. The only atoms of which the mass is in the neighbourhood of that obtained for the ions are those of argon (39·9), calcium (40·07), and potassium (39·1). There is a strong presumption in favour of the last named element and we shall assume that the common impurity which has given rise to the formation of positive ions in these experiments is a potassium impurity capable of emitting K^+ ions under the influence of heat.

Nevertheless, it remains incontestable that in some cases, at least, other ions can be emitted. We shall only mention the early experiments of J. J. Thomson (see above, page 95) who, working with the ions emitted by platinum in air at low pressures after prolonged heating, obtained ions both heavier and lighter than those found by Richardson. It is probable that in this case the ions are due to the metal or to the surrounding gas, although the phenomenon seems to be exceptional.

6. The influence of gases. In the preceding paragraphs we have examined the positive emission from metals in vacuo. As in the case of electronic emission the question arises as to what modifications will appear in the phenomena observed if a gas be introduced into the experimental tube.

The results obtained on this point are numerous but confused and rather contradictory, perhaps partly because up to the present scarcely any emissions have been examined except those from platinum and here again this metal may present complications greater than more refractory metals. The following are some of the results obtained: for the details reference should be made to Richardson's book.

Chronologically the first experiments were those of H. A. Wilson,* which were made in air at atmospheric pressure between two concentric cylinders of platinum heated by an external furnace to temperatures as high

* H. A. Wilson, *Phil. Trans.*, 1901, 197, 415.

as 1,400 degrees. The effects observed are complicated by the fact that a negative emission and also probably a volume ionization are superposed on the emission of positive ions. Nevertheless the author was able to ascertain from them that the saturation currents obtained satisfied Richardson's law.

Richardson * has re-examined the question with great care. A platinum wire was heated electrically in the neighbourhood of a sheet of the same metal. Both the tube which contained the electrode and the electrodes themselves were thoroughly cleaned before the experiments, and the wire was heated for a long time in rarefied oxygen in order to make the initial emission of positive ions disappear before the introduction of a small quantity of the gas to be examined ; oxygen, nitrogen, air, hydrogen or helium. The initial positive current having thus been enormously reduced (to a value of the order of 10^{-12} amperes at 721 degrees), the introduction of the gas definitely increased the current. The current diminished afresh when the gas was removed. The pressures of the gases examined did not exceed a few hundredths of a millimetre of mercury. The interpretation of the results was much easier than in the experiments of H. A. Wilson, for there was neither volume ionization nor emission of ions by the cold electrode. Moreover, in all cases the experiments were carried out at temperatures sufficiently low for the current to be practically zero when the heated filament was charged negatively : only the positive ions were involved.

Oxygen. If some inexplicable irregularities observed at high pressures and low temperatures are disregarded, it can be said that the saturation current at low temperatures is approximately proportional to the square root of the pressure, and at high temperatures to the pressure itself. These results assume, however, that the pressure does not exceed one millimetre of mercury. If results

* Richardson, *Phil. Trans.*, 1906, 207, 1.

valid for greater intervals of temperature are required it is necessary to adopt a formula of the type

$$i = \frac{a\sqrt{p}}{b + \sqrt{p}}$$

for temperatures less than about 900 degrees and for temperatures higher than this (1000 to 1200 degrees) the formula

$$i = \frac{ap}{b + p}$$

should be used. An endeavour may be made to give a theoretical interpretation of these results by assuming that the emission depends on the number of atoms of oxygen present at the surface of the platinum at each instant.

The law expressing the variation of the saturation current with temperature has also been investigated. At a pressure of 1·47 mm. for example, it is found that from 708 to 1,000 degrees the negative current is negligible with respect to the positive current. The two currents are equal at 1,230 degrees. Both currents are in sensible agreement with Richardson's law, with different values of the constants. Different wires give comparable results, which seems to prove that the emission actually comes from the platinum in oxygen and not from any accidental impurities. When the temperature is raised or lowered there is always a delay in the establishment of the new current conditions. Doubtless this delay is due to effects produced by oxygen which has diffused into the superficial layer of the platinum.

Other gases. Analogous phenomena are observed in nitrogen and in air. The currents at a given temperature are weaker than those in oxygen, and their saturation is more difficult. With helium, greater positive currents

are observed than with nitrogen though they are much less than those given by oxygen : their existence is interesting since it is impossible in this case to attribute them to a chemical action produced by the gas on the incandescent wire. In hydrogen, measurements of the positive current are difficult on account of the extreme slowness with which the steady state is established at a given temperature.

When a platinum wire has been heated for a long time in one gas the introduction of a second gas gives rise to an initial positive emission greater than the stationary value subsequently assumed. This phenomenon is produced with oxygen, nitrogen, helium, and hydrogen.

Few experiments have been made, as yet, to determine accurately the nature of the ions which carry the positive current in rarefied gases, once the initial period of relatively intense emission has passed. It is hardly possible to mention any experiments of this nature except the early experiments of J. J. Thomson already referred to (see page 95), and some experiments by Richardson. It may be that with old filaments, i.e., those which have been subjected to prolonged heating in a rarefied gas, the ions which carry the positive current are to a great extent derived from the gas, but accurate experimental data are still lacking on this point as well as on the relations which certainly exist between the positive emissions caused by a trace of gas and the corresponding variations of the contact potential difference.

Measurements of the mobilities of the ions emitted (H. A. Wilson, MacClelland, etc.) show definitely that particles of atomic dimensions are concerned. The determination of their exact nature is not rendered easier by the fact that if the ions are removed by a current of gas the mobility diminishes gradually to values which are very much less than the initial value, and this not only to an extent which is proportional to the diminution of temperature. It is not possible here to dwell on this diminution with time of the mobilities of the thermionic

ions. The phenomenon must be related to the analogous phenomenon observed with the gases from flames (MacClelland, Eugène Bloch, and so on), and must be reserved for special examination.

The emission from new filaments in gases. The preceding results relate to the emission of positive ions in gases from old wires, which have been heated for such a length of time that the fairly strong initial emission has practically disappeared. The investigation of this initial emission in gases, which evidently gives place to the experiments which are more immediately realizable, unfortunately leads to great complications. Nevertheless some of the facts observed are very remarkable.

Thus, Richardson * has shown that the decrease of the positive emission in the course of time which has been observed in a vacuum also occurs in air, but that it is much more rapid when the heated wire is maintained at a positive high potential. For example, a new wire heated to 925° C. under atmospheric pressure, gave a current at 40 volts which could be measured by the number 100 and which remained constant for 100 minutes. When the potential was raised to 760 volts the currents were :

Time in minutes	0	3	6	9	14	20	25	36	47	54	60	66
Currents ..	3570	1930	950	760	570	485	475	190	115	112	103	103

On returning to 40 volts, the currents were, at intervals of six minutes, 80, 84, 90, and 94. Moreover, the emission could be increased by charging the heated electrode negatively for a short time.

Additional observations made by W. Wilson † and Sheard ‡ are as follow. The positive emission can be increased by heating the wire temporarily to a high temperature while it is maintained at a zero or negative

* Richardson, *Phil. Trans.*, 1906, 207, 30.
† W. Wilson, *Phil. Mag.*, 1911, 21, 634.
‡ Sheard, *Phil. Mag.*, 1914, 28, 170. Sheard and Woodbury, *Phys. Rev.*, 1913, 2, 288.

potential. The increase is a definite but complicated function of the temperature to which the wire was raised at zero potential. In some cases the emission could be increased in this way to forty times its previous value.

It is clear that the removal of the ionizable matter by the electric field plays an essential part in the initial decrease of the positive emission. It even appears that in certain cases it can be asserted that the active matter is formed at temperatures which are already fairly high, so that the effect of heating in the absence of the field may be to increase the emission at a lower fixed temperature. On the other hand, too intense heating may provoke the distillation or the destruction of the active matter produced, whence the disappearance of the effects at the same temperature as before.

The curves showing the decrease of the positive emission with the time which Sheard has obtained with platinum wires at moderately high temperatures (between 654 and 714 degrees) in air, sometimes present irregularities similar to that shown in the second curve in Fig. 15, which relates to experiments in a vacuum.

These partial cessations of the velocity of decrease are again interpreted as in radioactivity by considering three successive substances to be involved, only the first and third of which are active in producing positive ions while the second serves merely as an intermediary in the transformation from the first to the third. Contrary to what occurs in radioactivity, however, the velocities of destruction vary with the temperature, and at the same time the shape of the curves changes.

The saturation curves also present complications analogous to those which have been observed in a vacuum. At low temperatures there is no saturation at all; at higher temperatures saturation is slightly easier. The complete interpretation of the facts remains obscure. According to Sheard and Woodbury it seems that in the emission from platinum wires it is necessary to assume

at least two different active substances, one of which is only formed after a fairly long time of heating. Indeed, if the Richardson curves be drawn with 1/T as abscissae and values of ($\log i - \frac{1}{2} \log T$) as ordinates, a single straight line is obtained initially, but eventually there are two straight lines making a definite angle with one another in the interval between 845 and 1,040 degrees. This confirms the results obtained with the curves showing the decrease of activity with the time.

CHAPTER IX

THE EMISSION OF IONS BY HEATED SALTS

1. Introduction. The increase in the conductivity of gases in the presence of heated salts was demonstrated for the first time by J. J. Thomson * in 1890. The conductivity was measured between two platinum electrodes in a crucible, into which a salt such as potassium or sodium chloride, potassium iodide, etc., could be introduced. A little later Arrhénius † showed that the conductivity of flames was strongly increased by the introduction of various salts. The efficacy of the salt increased with the atomic weight of the metal, at least so far as the alkali metals were concerned. Since then the employment of flames for the study of the conductivity of saline vapours has given rise to a large number of interesting experiments. Among the physicists who have contributed most to the clearing up of this question should be mentioned especially H. A. Wilson and his students in England and Moreau in France. Their method consisted essentially in placing two refractory electrodes in the flame of a gas burner of the Bunsen type and investigating how the conductivity of the pure flame was modified when various quantities of different salts were introduced, either by the spraying of a saline solution or by any other method. Some interesting laws have been obtained both by the comparison of the homologous salts of different metals at different temperatures, and by the measurement of the mobility of the ions produced. The influence of a magnetic field (the Hall effect), and that of an alternating electric field of variable frequency have also been examined.

* J. J. Thomson, *Phil. Mag.*, 1890, 29, 358 and 441.
† Arrhénius, *Ann. der Phys.*, 1891, 43, 18.

The conductivity of pure or salted flames constitutes a subject of sufficient importance to merit separate study which cannot be undertaken here, and although this subject is closely connected with thermionic phenomena properly so-called we shall not develop it. The reader desirous of further information is referred to the book by H. A. Wilson entitled *The Electrical Properties of Flames and Incandescent Solids* (University of London Press, 1912), or to the papers by Moreau,* and we shall only study the phenomena of the electrical conductivity caused by heated salts in the absence of flames and of their chemical effects.

The first systematic investigation of the problem thus restricted was undertaken by H. A. Wilson † who sprayed solutions of various salts into the space between two platinum cylinders (0·3 and 0·75 cm. in diameter) heated from the outside. Saturation was difficult but was nevertheless attained at 1,000 volts. Numerous irregularities in the results seemed to be due to the chemical action between the salts and the water vapour. The greatest currents were obtained with potassium iodide, and were measurable with a galvanometer at as low a temperature as 300 degrees. With all the salts examined, the current became independent of the temperature at about 1,400 degrees, and corresponded approximately to that which would have been carried in electrolysis by the same quantity of salt. Everything happened as if all the metallic atoms present were transformed into positive ions which were absorbed by the cathode as soon as they arrived. The only salts examined were those of the alkalies.

Beattie ‡ has investigated the influence of a large number of mineral compounds on the conductivity of the air

* Moreau, *Annales de Chimie et de Phys.*, 1903, 30, 1, etc. ; *Bull. de la Soc. Scient. et Méd. de l'Ouest*, 1906, 15, no. 2 ; 1906, 15, no. 4, *Ions, Electrons et Corpuscles*, 2, p. 540.

† H. A. Wilson, *Phil. Trans.*, 1901, 197, 415.

‡ Beattie, *Phil. Mag.*, 1899, 48, 97 ; 1901, 1, 442.

between the plates of a plane condenser at about 300° C. The halogen compounds of zinc are particularly active. The phenomena have been examined in a similar manner by Garrett and Willows,* Garrett,† Schmidt and Hechler,‡ Schmidt,§ and others. A large number of substances become active at about 400 degrees, the majority giving ions of both signs but some only positive ions. The case of potassium iodide has given rise to some discussion. It seems that the conductivity sometimes exhibited with this salt at about 300 degrees (H. A. Wilson) must be attributed to a chemical action between the salt and a trace of water vapour. If care is taken thoroughly to dry the gas the conductivity becomes inappreciable at this temperature (Kalandyk||).

The explanation of these relatively early experiments is somewhat doubtful since the ions may have their origin in a volume ionization of the vapour between the two heated plates, or they may be due to an emission by the electrodes under the action of the vapours of the salt as well as to an emission by the salt itself. Sheard¶ has thrown some light on this question by making a detailed investigation of cadmium iodide. By using a cooled electrode to collect the ions and by making the vapour of the salt pass through an intense electric field before examining it he has been able clearly to distinguish two effects: the emission of ions by the salt and the volume ionization of the vapour.

J. J. Thomson** has examined a large number of mineral substances in ordinary air at temperatures much higher than the foregoing. Certain compounds, the oxides for example, lose only negative electricity, others only

* Garrett and Willows, *Phil. Mag.*, 1904, 8, 437.
† Garrett, *Phil. Mag.*, 1907, 13, 728; 1910, 20, 577.
‡ Schmidt and Hechler, *Verh. der Deutsch. Phys. Ges.*, 1907, 9, 39.
§ Schmidt, *Ann. der Phys.*, 1911, 35, 404; 1913, 41, 673.
|| Kalandyk, *Proc. Roy. Soc.*, 1914, 90, 638.
¶ Sheard, *Phil. Mag.*, 1913, 25, 370.
** J. J. Thomson, *Proc. Camb. Phil. Soc.*, 1906, 14, 105.

positive ; in the latter class are chlorides and phosphates. Aluminium phosphate gives particularly high currents.

The majority of the preceding experiments can only be regarded as interesting from the historical point of view : in particular, they have provided the necessary information for the choice of the salts which can be investigated with the greatest advantage. In modern experiments a small quantity of the substance under examination has usually been placed on a wire or on a metallic sheet heated electrically and placed opposite a cold electrode. The arrangement is thus the same as with Wehnelt cathodes, In general the current only passes in a vacuum or in a gas if the heated electrode is at a higher potential than the other, which proves that the positive ions play a preponderating part. The ions emitted arise either from the heated salt or perhaps from an action of the salt on the metallic support ; as we shall see, the latter hypothesis is very much less probable. As regards the intervention of the other electrode or of volume ionization, they are eliminated by the experimental arrangement which has been adopted.

2. Variations with the time. The saturation current is more easily obtained at low pressures and at relatively low temperatures. It is always more difficult than with metallic electrodes, but it is possible to get near enough to it in all cases to be able to undertake the investigation of the variation of the emission with time or with temperature.

The variations of the emission with time, when the temperature and applied voltage remain constant sometimes present curious characteristics. This is particularly the case with zinc iodide (Garrett and Willows, and later Garrett, loc. cit.), aluminium phosphate (Garrett), and so on. The curves obtained with the latter salt heated to about 1,200° C. in an atmosphere of carbon dioxide under a pressure of 0·5 mm. of mercury, are

reproduced as an example of the results. It will be observed that the curve suddenly falls after an initial very sharp ascent, only to reascend once more. For greater clearness the final phase has been represented with a larger scale of ordinates above the main curve. The curve as a whole is very well represented by an equation of the type

$$i = a(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + b(1 - e^{-\lambda_3 t}).$$

It seems as if there were formation without emission (a, λ_2) of an active product which rapidly disappears

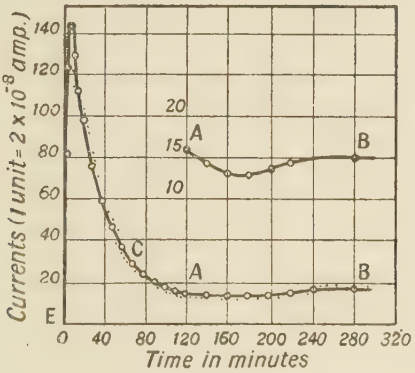

FIG. 18

(a, λ_1), together with the independent inactive formation of a product (b, λ_3) which disappears very slowly with the emission of ions.

Complications of the same nature have been observed by Schmidt, Richardson, and Horton with zinc iodide, aluminium chloride, the chloride, bromide, and iodide of cadmium, sodium sulphate, calcium iodide, and so on, in nitrogen and in air. Sheard has examined the iodide of calcium in detail from this point of view. It is almost beyond doubt that the complicated variations of the

emission with the time which are observed in many cases are due to chemical reactions, but the exact nature of these reactions is still open to question. In the case of cadmium iodide for example, it is clearly established that water vapour, even when present only in traces, has an effect on the emission. It is also probable that appreciable quantities of a little-known sub-iodide are formed, the presence of which strongly influences the emission. Finally, it must not be forgotten that the extreme sensitivity of the electrometric method of detecting the liberation of exceedingly small electrical charges does not facilitate the interpretation of the experiments. Certain chemically pure salts of commerce, the purity of which has been checked by delicate chemical tests, may nevertheless retain traces of other salts sufficiently to modify very appreciably the trend of their thermionic emission. A very striking example of this is furnished by aluminium phosphate. J. J. Thomson found one specimen of this salt to be much more active than the others, which seemed to imply the presence of an accidental impurity. Richardson, supposing that the impurity might be an alkaline salt (see later), prepared synthetically a specimen of aluminium phosphate as free from alkali as possible. As a matter of fact the emission from this was found to be very small, and after heating for a few minutes it fell to a value 150 times smaller than the emission from the " pure " aluminium phosphate of Kahlbaum. It may even be questioned, in many cases similar to this, whether the emission observed is not entirely due to a trace of a very active impurity, which may be liable to disappear more or less readily in the course of time by distillation or by some other process.

3. Variations with temperature. The foregoing observations, and particularly the variation of the emission with time, make the investigation of the variations with temperature rather difficult. Nevertheless, this investigation has

been carried out in several cases, and it has been demonstrated that Richardson's law is always satisfied. For example, such is the case with aluminium phosphate (Garrett), cadmium iodide (Schmidt), calcium fluoride and the iodides of calcium and strontium (Richardson), and zinc bromide and the iodides of cadmium and zinc (Kalandyk). For zinc iodide in air at 2·5 mm. pressure, Garrett found that at a temperature of 250° C. the constants of Richardson's formula changed in value abruptly, probably on account of a change in the active substance. The constants b of the formulae are comparable in magnitude with those obtaining in the positive emission from metals and smaller than those which correspond to the electronic emission.

4. The influence of the pressure and the nature of the gas. These influences are very complex, and for a detailed account of the facts reference should be made to Richardson's book, or, better still, to the original papers.

As regards the influence of pressure it can be said that in general, when the pressure is increased from very small values, an increase in the positive current is first observed, and then, after a well-defined maximum, there is a diminution at a rate slower than the initial increase. The position of the maximum depends on the temperature and also, of course, on the nature of the salt. Further, the effect observed cannot be attributed to ionization by collision. It has been established for aluminium phosphate (Garrett), for the phosphates of sodium and lithium (Horton*), and for sodium sulphate (Richardson †). Horton has examined aluminium phosphate and the ortho- and pyrophosphates of sodium with particular care.

Richardson heated the salts in a fairly long platinum tube, containing an axial electrode, instead of heating

* Horton, *Proc. Camb. Phil. Soc.*, 1910, 16, 89; 1911, 16, 318; *Proc. Roy. Soc.*, 1913, 88, 117.

† Richardson, *Phil. Mag.*, 1911, 22, 676.

them electrically on a sheet of platinum. In this way he ascertained that the method of heating has a very great effect on the results obtained. The curves showing the variation of the current with the pressure which he obtained with the sulphates of sodium, beryllium, and barium, and with aluminium phosphate differ entirely from those which had been previously published. It is probable that the chemical actions between the salt or its vapours and the electrodes are much more marked with this arrangement than with the usual apparatus, but the question is still far from being completely cleared up.

5. The nature of the ions emitted. It is obvious that as in the case of metals the question of the chemical nature of the ions emitted by heated salts is one of the most important which can arise. To answer it, it is again necessary to have recourse to the measurement of the ratio e/m of the charge to the mass of the particles emitted, and this measurement is made by the methods previously indicated (Chapter VIII). The electric atomic mass M of the ions is thus obtained.

The first measurements were made on a fairly large number of alkaline salts in vacuo by Richardson,* using the slit method (page 95). The salts examined were the sulphates of lithium, sodium, potassium, rubidium, and caesium. The essential result, which has been placed beyond doubt by a very large number of experiments, is that the positive ions emitted are *charged metallic atoms*. In some cases these atoms may belong to a metal other than that forming the salt, on account of the presence of very active impurities. Thus, in the case of lithium sulphate during the first few hours of heating ions of an electric atomic mass in the neighbourhood of 40 are observed, these being probably potassium ions. But in the majority of cases, and in all cases when the heating is sufficiently prolonged, the ions appear to be those of the

* Richardson, *Phil. Mag.*, 1910, 20, 981 and 999.

metal which constitutes the salt. The following table, in which all the results are collected, clearly demonstrates this fact. The figures in the last two columns differ by quantities less than the possible experimental errors. The ions emitted are therefore indeed those of the metal forming the salt.

Substance	Duration of Heating in Hours	M Observed	Mean Value of M	Atomic Mass of the Metal
Li_2SO_4	12	5·5	6·2	7·00
	44	5·57		
	52	7·43		
Na_2SO_4	8	23·4	22·5	23·0
	24	22·5		
	13	22·0		
	15	22·0		
K_2SO_4	0	37·0	36·5	39·0
	6	37·0		
	24	37·0		
	36	35·5		
	42	36·3		
	60	36·3		
Rb_2SO_4	—	96	96	85·5
Cs_2SO_4	0	95	140	132·8
	18	163		
	23	163		

A complete investigation of the salts of the alkaline earths has been made by Richardson, and especially by Davisson.* Here again it seems probable that, in general, the ions emitted belong to the metal of the salt. A very

* Davisson, *Phil. Mag.*, 1912, 23, 121 and 139.

interesting fact is that in no case were divalent ions obtained, which is contrary to what occurs in electrolysis with metals of this group; all the ions observed were metallic atoms which carried only one elementary charge. In the case of the salts of barium (sulphate, chloride, and fluoride) and of strontium (sulphate, chloride, fluoride, and iodide) there is no doubt about the chemical nature of the ions emitted, although an emission of potassium ions was observed to be superposed on the others in some cases: the atomic mass of potassium, in fact, differs too much from that of these two metals for any confusion to be possible. The case of the salts of calcium is more open to discussion since the atomic weights of calcium (40·1) and potassium (39·1) are very close together. The same difficulty arises with magnesium (atomic weight 24·3), when it is a case of distinguishing it from sodium (atomic weight 23·0). In all cases it is possible to assert that here again there is never an emission of *Ca* or *Mg* ions carrying a double charge.

The salts of zinc have furnished the only example of polyvalent ions so far observed. The atomic weight of zinc being 65·4, the electric atomic mass should have exactly this value if the ions were monovalent, and one-half this value (32·7) if the ions were divalent. Zinc iodide at the commencement of the heating yields values comprised between 28·8 and 34·2.

The values of the atomic masses of the ions emitted sometimes varies very definitely with the time of heating. An example of this is found in the case of cadmium iodide, which has given the results shown in Fig. 19. The times in minutes have been used as abscissae and the values of the electric atomic masses as ordinates. The successive temperatures to which the salt has been heated in the course of the experiment have also been marked. It will be observed that the temperature has been raised progressively; this is a precaution rendered necessary by the regular decrease of the effects with time. It will be

seen that at the beginning of the heating the ions emitted are cadmium ions; these are subsequently replaced by ions of potassium, and later by sodium ions. The two last named arise from alkaline impurities mixed with the principal salt.

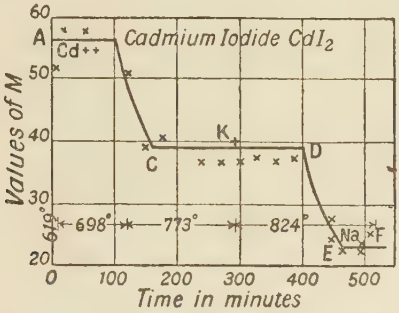

FIG. 19

The salts of the other groups of metals give less definite results. Many of them appear to emit principally ions of potassium or sodium, no doubt because the thermionic activity of the alkaline impurities greatly preponderates over the characteristic activity of these salts. Such is the case with numerous salts of iron, aluminium, silver, lead, copper, and so on.

It has been seen in Chapter IV that the presence of a small quantity of gas in the tube in which the thermionic experiments are carried out can give rise to an appreciable increase in the emission. It may be asked whether the nature of the positive ions emitted remains the same in spite of this, or whether the effect of the gas is to modify them also. As Davisson has shown, the first alternative is the correct one. The substance examined was aluminium phosphate, which emits principally sodium ions. The electric atomic mass of the ions does not appear to change when carbon dioxide, air, or hydrogen is introduced into the tube, even though it be in such

quantities as to exert the maximum pressure at which the experiments can be conducted. These pressures, however, are not very high on account of the disturbances which arise from ionization by collision ; they are of the order of 1·4 mm. of mercury for hydrogen, and so on.

6. The mobilities of the ions emitted by heated salts. The measurement of the mobilities of the ions emitted by heated salts affords another method of ascertaining their nature. Unfortunately, this method is much less efficacious than the preceding one, because the measurements are usually made by removing the ions in a current of gas and examining them subsequently at a temperature very much lower than that at which they are produced. This method has been employed by Garratt and Willows, but it has been developed in particular by Moreau. Among the interesting results obtained by this author must be mentioned especially the fact that the mobilities observed when the temperature of the gas is sufficiently reduced become less and less and finally tend towards those of the ' large ions ' of phosphorus. It is very probable, therefore, that the ions emitted by the salt gradually become heavier by becoming surrounded by relatively important material agglomerations, so that the measurement of the mobilities only gives very indirect information concerning their initial chemical natures.

We shall not persist in the examination of this question, which is connected too closely with other subjects, such as the investigation of large ions and the conductivity of the gases from flames, which are foreign to the one we are studying.

In concluding the study of the thermionic emission from heated salts it may be remarked, in the first place, that the most active salts are those of the most electropositive metals, that is to say, those of the alkali metals. Among these the activity increases with the atomic weight of the

constituent metal. The activity of the alkali metals is such that in many cases the presence of an alkaline impurity completely conceals the characteristic emission of the salt itself, if this exists. Finally, in spite of certain differences, it is impossible not to be struck by the similarities between the thermionic emission from heated salts and the positive emission from heated metals. As we have seen, the latter is also frequently due to alkaline impurities, and it is very possible that in certain cases the two phenomena should be identified and attributed to a single cause.

CHAPTER X

THE APPLICATION OF THERMIONIC PHENOMENA TO THE MEASUREMENT OF HIGH VACUA AND TO THE RECTIFICATION OF ALTERNATING CURRENTS

1. Introduction. Thermionic phenomena, and especially the emission of electrons in a vacuum, have already received a large number of practical applications. Some of these have even assumed such proportions that they now give rise to industrial manufactures, and it is probable that this movement is only commencing.

Among these applications we may mention:

1. Certain improvements in the theory of the electric arc which have led to considerable practical improvements in several cases.
2. The Coolidge tube for the production of X-rays, which utilizes the pure electronic emission in a perfect vacuum, and which affords the best source of X-rays available at the present time.
3. Three electrode valves (audions, pliotrons, dynatrons, and so on), the employment of which in wireless telegraphy and telephony has expanded to such a large extent in the last few years, and which have enabled transmission and reception to be improved to such a point that their appearance can be characterized as a veritable revolution. In addition, it appears probable that their employment as instruments for investigation and measurement in the many other applications of electricity will continue to increase.

4. The measurement of very high vacua by gauges called 'ionization gauges' which allow the quantitative investigation of the very rarefied gases that can be furnished by modern vacuum pumps.
5. The rectification of alternating currents by the utilization of the unipolar character of the thermionic phenomena.

The examination of the first three applications will not be entered into here as they have been described in other volumes of this series.* We shall be content to study the last two of the applications, namely, the measurement of high vacua and the rectification of alternating currents. This last application especially is one of those which were first proposed, and it is the one which is most apparent. In addition, it has developed greatly during the last few years.

2. Ionization gauges. Vacua of the order of one thousandth of a millimetre of mercury, and even of one ten-thousandth of a millimetre, can be measured by the classical method of the McLeod gauge, provided that the pressure of the mercury vapour (which is itself of the order of a micron at ordinary temperatures) is not taken into account. But it has been seen above that thermionic phenomena can be profoundly changed by the introduction into the experimental tube of a gas under a pressure comparable to one micron, and the progress of vacuum technique enables pressures which are one hundred, one thousand, and even ten thousand times less than this to be attained at the present time. It has therefore become necessary not only to obtain these very high vacua but also to measure them by new and sufficiently sensitive methods.

* For the application to the electric arc see *L'Arc Électrique*, by M. Leblanc fils; for the Coolidge tube, *Les Rayons X*, by M. de Broglie (English translation, *X Rays*, published by Methuen); for three electrode valves, *La Lampe à trois électrodes*, by C. Gutton.

Several of these methods, based on the molecular properties of rarefied gases (viscosity and thermal conductivity), are foreign to our subject,* but there is another method which employs precisely the sensitivity of thermionic phenomena to traces of gas, and this will be briefly described.

We have already seen (page 75) that by placing an incandescent tungsten filament surrounded by a cold electrode inside a vacuum tube, the presence of a trace of gas can be revealed by the close study of the shape of the saturation curve in a portion of the intermediate region which corresponds to the 3/2 power law. The proof of the existence of a trace of gas becomes much easier if a second cold electrode is introduced into the tube. This is then a three electrode tube consisting of : (*a*) the incandescent filament ; (*b*) a second, cold, filament forming a grid round the first ; (*c*) a cylinder (or plate) itself surrounding the grid. These three electrode tubes which have rendered such great services in wireless telegraphy are found here also to be superior to the simple tubes with two electrodes.

Their adaptation to the measurement of high vacua, first proposed by Buckley † has been improved by Dushman and Found.‡ The last-named used a grid of tungsten wire and a plate of molybdenum. For the measurement of a pressure of less than one micron of mercury (about one bar) the incandescent filament emits an electronic current of between 10 and 20 milliamperes. The grid is raised to about 250 volts, and the plate is at about —20 volts with respect to the grid. If the vacuum is perfect no ionization by collision is produced between the grid and the plate in spite of the considerable kinetic energy of the electrons projected by the filament, and the plate does not receive any current. If, on the contrary, the tube

* In this connexion see *La Technique du Vide*, by L. Dunoyer.
† Buckley, *Proc. Nat. Acad. Science*, 1917, 2, 683.
‡ Dushman and Found, *Phys. Rev.*, 1920, 15, 133.

contains a trace of gas, the positive ions produced by the collisions of the electrons will reach the plate, and the current between the grid and the plate will enable the degree of vacuum to be measured.

The gas chosen for the calibration of this gauge was argon. The proportionality of the currents to the pressure was verified by other methods in the interval between 50 bars and 0·001 bar. The validity of the same linear law is assumed at lower pressures. Calibration with the following gases leads to similar results: nitrogen, mercury vapour, carbon dioxide, hydrogen, and water vapour.

The necessity of a calibration in order to ascertain the coefficient of the linear law is a complication inherent in the method, but it is difficult at the present time to exceed the sensitivity attained.

3. The rectification of alternating currents. As has been mentioned in Chapter I (page 3) Fleming was the first to conceive the idea of utilizing the Edison effect for the rectification of alternating currents. Indeed, it is known that an incandescent filament raised to a sufficiently high temperature in a good vacuum emits practically only negative electrons and no positive charges. If, therefore, an alternating potential difference is established between the filament and a cold electrode placed near to it, a current will pass through the vacuum during the current phase in which the filament is at a potential lower than the cold electrode; on the other hand, the current will be zero during the opposite phase. During the first phase the current is carried by the electrons emitted by the filament travelling towards the auxiliary electrode: it is a current of negative electricity. This current is equivalent to a current of positive electricity directed in the opposite sense, namely, towards the filament. Further, if an apparatus for measuring continuous currents is placed in the external circuit, this apparatus will indicate a current

passing through the tube from the cold electrode to the filament ; its direction is the same as if it were produced by a battery of accumulators with the negative pole connected to the filament. In addition, it is intermittent, since it only passes for half of each period, and, in general, the measuring instrument will indicate its mean value.

It is interesting to recall that Fleming had foreseen from the beginning the part that this rectifier or ' Fleming valve ' might be able to play in wireless telegraphy. Indeed, detection in wireless telegraphy consists in the rectification of an alternating current captured by the receiving antenna, and well-designed thermionic rectifiers function with as much security for the very weak, very high frequency currents of wireless telegraphy as for the alternating currents of greater strength or very much lower frequency which are normally encountered in the industrial applications. This particular application will not be developed here, as the employment of thermionic tubes as detectors has only assumed its present large proportions since the discovery of the three electrode valve, and the operation of these valves is the subject of Gutton's book. We shall confine ourselves to the study of two electrode tubes, which can be used only as rectifiers of alternating currents, and we shall specially consider them in the very important case of pure electronic emission.

The American physicists were the first to make, for certain practical purposes, alternating current rectifiers based on the use of the pure electronic emission in a very high vacuum. They proposed the name ' kenotron ' for them, to recall their characteristic property, which is to function in a perfect vacuum. We shall employ this convenient expression and examine in some detail the way in which these instruments function.

4. The kenotron. Numerical data. In order to fix our ideas, let us suppose, as is generally the case, that the incandescent electrode, heated by a source independent

of the current to be rectified, is a tungsten filament. If all the precautions previously mentioned have been used in the production of the vacuum, the electronic emission from the tungsten will be in accordance with Richardson's law, $i = aT^{\frac{1}{2}}e^{-\frac{b}{T}}$ and the coefficients a and b of the formula which expresses this law will have the numerical values :*

$$a = 23{\cdot}6 \times 10^9 ; \quad b = 52{,}500,$$

provided that the electronic current is measured in milliamperes per square centimetre. By means of this formula it is possible to calculate *a priori* the electronic currents which will be obtainable from a filament with a given surface at various temperatures. The following table † has been prepared in this way :

T absolute	i per square cm.
2,000	4·2 milliamperes
2,100	15·1
2,200	48·3
2,300	137·7
2,400	364·8
2,500	891·0
2,600	2,044·0

The choice of the incandescent filament is guided by considerations of the ease of manufacture, of the expense of the auxiliary energy necessary to raise it to incandescence, and also, as will be seen, of the mechanical resistance. The temperature to which the filament will be raised must be chosen in such a way that the electronic current is as

* See the data on page 33.

† Dushman, *General Electric Review*, 1915, 18, 156.

intense as possible without the life of the filament being unduly shortened. In practice, whatever the diameter of the filament, it is generally advantageous not to exceed a temperature of 2,500 degrees absolute, if it is desired to prolong the life of the filament up to 1,000 hours. Under these conditions, with the usual filaments, which have diameters varying from a few hundredths to several tenths of a millimetre, electronic emissions are obtained ranging from a few milliamperes to several hundred milliamperes.

The kenotrons constructed up to the present are of several different types: some are designed for the rectifications of the relatively small alternating voltages between 200 and 10,000 volts, yielding currents with these voltages which range from 10 or 15 milliamperes to 400 milliamperes. Others are adapted to very much higher alternating voltages, being able to take up to 100,000 volts and giving currents up to 100 milliamperes. Instruments of the latter type are particularly convenient, when used with a suitable condenser, for supplying Coolidge tubes of high radiation output. Those of the former type are capable of a host of applications, such as supplying Geissler tubes, and so on. We shall see later that if it be desired to use thermionic methods for the rectification of alternating currents greater than a few tenths of an ampere the kenotrons must be replaced by tubes containing a suitably chosen gas.

5. The shape of the rectified current wave. Let us examine the characteristic properties of a kenotron. To this end let us assume that the incandescent electrode is maintained at its normal working temperature. If there be applied to the kenotron a voltage which, in the first place, will be assumed to be continuous and such that the cold electrode is at a higher potential than the filament, it will be possible by increasing the voltage to obtain a saturation curve. We know that this curve commences

with an ascending portion which satisfies the 3/2 power law

$$i = kV^{\frac{3}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (29)$$

and which is followed by the saturation phase with a constant current. Experiment has shown that with the types of kenotron constructed up to the present time the constant k of the preceding formula is between 5×10^{-3} for high voltage instruments and 250×10^{-3} for kenotrons to be used with lower voltages. In other words, for a fall of potential of 100 volts in the kenotron, the current yielded

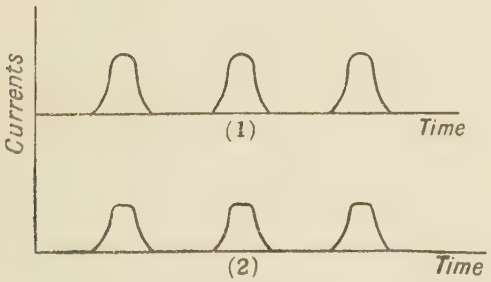

FIG. 20

varies from 5 to 250 milliamperes, if it be supposed that the saturation phase is not yet attained with this voltage. In addition, it has been possible to confirm that these values of the constant k are in good agreement with the values predicted by the theory (see the formula 25 on page 61), in the case where the calculation is made possible by the shape of the electrodes.

From this it is possible to predict the shape of the current wave when rectified by the kenotron. To take an example, if a sinusoidal voltage be applied, and if the maximum voltage is insufficient to saturate the current, this will continue to satisfy the 3/2 power law during the whole of

the time of rectification. The curve showing the rectified current will therefore be of the type shown in curve (1) in Fig. 20. During the half periods when the potential of the filament is higher than that of the cold electrode the current is zero; during the other half periods it varies directly as the 3/2 power of the ordinates of the voltage sine wave.

On the other hand, if during the course of the alternations the voltage becomes large enough to reach and exceed the saturation value, the rectified current curve will be similar to curve (2) of Fig. 20. The ascending and descending portions during which saturation is not attained will continue to satisfy the 3/2 power law, but these are separated by a horizontal portion which corresponds to the saturation phase. In general, this case is a less advantageous mode of functioning than the first; the latter should therefore be regarded as the normal method of use.

These predictions relative to the current curves of kenotrons have been entirely verified by experiment. Some striking examples of this are to be found in the paper by Dushman which has been mentioned previously. By means of an oscillograph this author has traced the curves giving the voltages applied to the terminals of a kenotron at the same time as the rectified current curves, working with an industrial supply at a frequency of 60 cycles per second. The curves obtained confirm the predictions of the theory down to the smallest detail.

6. The fall of potential in the kenotron. We will next examine the important question of the fall of potential in the kenotron, a question which is closely connected with that of the efficiency. In order to fix our ideas we will take the example of a kenotron for use with a Coolidge tube, designed to rectify an alternating voltage of 100,000 volts, for which the constant k in formula (29) might have the value 100.10^{-3}, and we will suppose that the maximum

current which this kenotron can yield is 100 milliamperes. The power furnished at the instant of this maximum is 10 kilowatts ; at the present time it is difficult to go beyond this.

In the first place, let it be observed that according to formula (29), so long as the maximum current of 100 milliamperes is not attained the voltage across the terminals of the tube will not exceed 100 volts. If the voltage across the terminals does exceed this value on account of the action of the supply circuit, the 3/2 power law will cease to be applicable and the increase in voltage will not be accompanied by any increase in the current. There will only be an increase in the power expended in the kenotron itself without any increase in the power available in the external circuit ; in other words, the efficiency will be diminished. It is advantageous, therefore, to keep the conditions under which the external circuit functions within such limits that the voltage across the terminals does not exceed 100 volts, so that the 3/2 power law remains applicable to it. As has been stated above, these are the normal working conditions, and it is endeavoured to depart from them as little as possible.

To take an example, let us suppose that the circuit of the high voltage alternator, the current from which is to be rectified, contains a high resistance placed in series with the kenotron concerned ; this will be called the 'utilization resistance'. We will denote the electromotive force of the alternator by E and the utilization resistance by R, and we will assume that the internal resistance of the alternator is entirely negligible with respect to R. It follows from Ohm's law that the fall of potential along the utilization resistance is iR, and hence the voltage across the terminals of the kenotron is

$$V = E - iR.$$

Formula (29) shows that if this voltage does not

exceed 100 volts it is related to the current by the equation

$$i = k(E - iR)^{\frac{3}{2}}.$$

It follows from this that if the utilization resistance be progressively diminished the current yielded will increase. In this way it will reach its saturation value of 100 milliamperes. When this occurs the current i cannot further increase, even if R is further diminished. The foregoing formula then ceases to be applicable and the voltage across the terminals of the kenotron progressively increases from that value which corresponds to saturation. In fact, the whole of the voltage from the alternator which is not absorbed by the utilization resistance automatically goes across the terminals of the kenotron. If this phenomenon is allowed to proceed to a large extent—if, for example, by some mistake the utilization resistance is short-circuited—the whole of the voltage of the source will fall across the kenotron, and consequently the whole of the power of the source will be expended in the form of heat in the kenotron. In general, the result of this will be the fusion or the deterioration of the anode, since the power brought into action in our example is 10 kilowatts. This is rather a serious matter; to guard against it a safety device must be employed which will cut off the current in the case of an accidental short circuit before the voltage across the terminals of the kenotron shall have assumed a dangerous value.

The question of the efficiency of a kenotron is very closely connected with the foregoing considerations. In fact, the power lost in the kenotron is given by

$$W = Vi = kV^{\frac{5}{2}}$$

so long as the working is normal. In our example the maximum value of this power loss in 100 volts $\times$ 100

milliamperes, or 10 watts. To this power, which is employed in heating the anode (since it is carried by the electrons which strike the anode and are absorbed thereby), it is necessary to add the power used in heating the filament with an auxiliary battery of accumulators. The heating current of the filament varies with the type of kenotron from 2 to 10 amperes, and it is supplied by the battery at about 10 volts. Thus the power expended in the form of heat in the filament is of the order of 100 watts, but it must be observed that on account of radiation from the filament some of this heat also can be transferred to the anode. Altogether, so long as the operation of the kenotron remains normal the efficiency is excellent: in the example we have taken it is about 99 per cent (100 watts lost on 10 kilowatts). If there is any departure from the normal working conditions not only does the efficiency diminish but, as we have seen, the largely increased heating of the anode may become dangerous to the apparatus. Moreover, when the anode, which is constructed of a refractory metal in order partially to avert this danger, reaches too high a temperature it also becomes a source of electrons; the current will cease to be unipolar and the rectification will become less and less perfect. On the contrary, so long as the working remains normal the rectification also remains satisfactory at all frequencies. Electronic rectifiers appear to be entirely free from inertia even when the frequencies attain those of the order used in wireless telegraphy.

7. Electrostatic effects in the kenotron. It has been seen that in kenotrons as at present made the alternating voltages brought into action are always high, and are reckoned in thousands or in tens of thousands of volts. It would appear at first sight that there would be little danger with these voltages from the point of view of their electrostatic actions, since in the normal working of the kenotron the voltage across the terminals of the most

powerful kenotrons does not exceed a few hundred volts. It should not be forgotten, however, that this working is intermittent, and that in every alternation the current only flows during half the period. It is during this half period, which can be called the useful half period, that the foregoing arguments are applicable, and that the voltage across the terminals falls to a few hundred volts. During the other half period, which can be called the half period

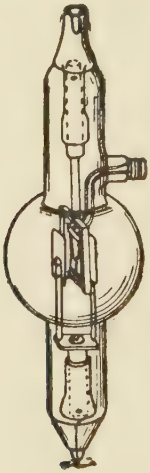

FIG. 21

of rest, the current falls to zero. At this instant no power is expended in the apparatus but, on the other hand, it behaves as an infinite resistance, which means that all the voltage of the source is thrown across its terminals. Thus during every period of the alternating current the voltage across the terminals of the kenotron passes regularly from a value of the order of a few hundred volts to a value of the order of tens of thousands of volts. As the electrostatic action which two conductors exert on each other varies

proportionally to the square of the difference of potential between them, it follows that the mechanical forces exerted on the filament during the half period of rest are not at all negligible. If the filament is too fine or insufficiently supported it will commence to vibrate with a frequency equal to that of the current which is being rectified, and a rapid deterioration, or even a rupture of the filament may result. For this reason designers have been led to search for methods of construction as robust as possible, especially in the case of kenotrons to be used at high voltages. One type of kenotron manufactured by the General Electric Company of America for supplying Coolidge tubes is shown schematically in Fig. 21. The filament, fairly rigid in itself, has been given the form of a V, and is supported by a frame for the purpose of increasing its mechanical resistance.

8. Circuits used for rectification. The circuits which have been used for the rectification of an alternating current vary with the application in view and are fairly numerous.

In many cases it is sufficient to connect the alternating source to the terminals of a condenser of sufficiently large capacity, inserting a kenotron in one of the two connexions. The condenser gradually charges up till the difference of potential across its terminals becomes equal to the maxumim electromotive force of the source.* If the insulation of the condenser is good enough the current yielded will then fall to zero, or rather will be reduced to a value necessary to compensate for the losses in the condenser. The condenser in turn will be able to serve as a source of continuous high potential and this source will maintain a constant electromotive force which, in practice, is little less than that of the supplying alternator, on condition that: (*a*) the current taken from it does not

* This source may be, of course, the secondary of a static alternating current transformer.

exceed that which the kenotron normally supplies : (*b*) the condenser has so large a capacity that the difference of potential at the terminals has not time to decrease to an appreciable extent during the half period when the kenotron yields no current. When it is desired to obtain currents of several milliamperes this last condition involves condensers of relatively high capacity, several tens of microfarads for example. Moreover, the insulation of the condenser must be designed to support the high tension of the source of supply. An arrangement of this type is suitable, for example, for supplying a Coolidge tube or

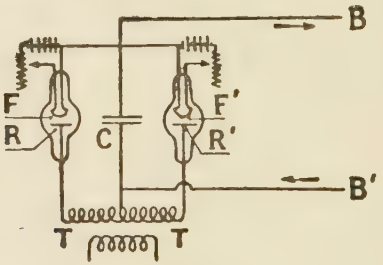

FIG. 22

any other tube designed for the production of a discharge in a rarefied gas.

The preceding arrangement has the great disadvantage of utilizing only one of the two alternations of the source. It is advantageous from every point of view to use both half waves, and this can be done by the employment of two kenotrons, or, what comes practically to the same thing, of one kenotron with two anodes placed symmetrically with respect to the incandescent cathode. Fig. 22 shows the circuit which can be adopted in the case of two identical kenotrons. The filaments of the two instruments are assumed to be heated by two independent batteries of accumulators. The source of alternating supply is the secondary of a transformer TT, the mid point

of which is connected to one of the wires B of the load circuit. The two terminals of the transformer are connected to the two anodes of the kenotrons, and the cathodes of these are connected to each other and to the wire B of the external circuit. Under these conditions it is easily seen that during one of the alternations the first kenotron only passes a current, and that on the contrary this is only done by the other one during the other half period. The rectified current in the external circuit again exhibits variations which depend on those of the supply voltage,

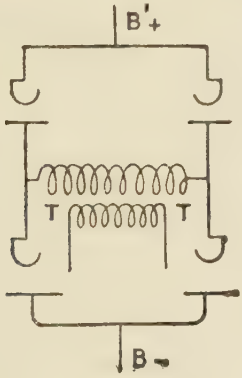

FIG. 23

but there is no interruption. Here again in order to reduce these variations and to obtain a current which is practically continuous, a large condenser C is put across the terminals of the load circuit. In fact it is this which really acts as the continuous source.

This circuit again has one disadvantage ; it only makes use of half the maximum alternating voltage of the source for each kenotron and consequently for the external circuit. It is possible to utilize the whole of this voltage by employing an arrangement similar to that of Fig. 23, in which is shown the rectification of the alternating

current from a transformer by means of four identical kenotrons. The condenser which it would be necessary to place across the terminals BB′ of the external circuit in order to decrease the fluctuations of the rectified current is not shown in the figure.

9. Gas rectifiers. The perfect vacuum rectifiers or kenotrons which have just been studied have the advantage that they are capable of being manufactured with such regularity that they are interchangeable or can be connected in parallel. With their aid, grouping them in parallel, we may expect to be able to obtain rectified currents of such powers as are used industrially, for example, for the long distance transmission of energy.

On the other hand individual kenotrons have the disadvantage that they do not permit of a current yield greater than a few hundred milliamperes at the most, though it is true that this is rectified high voltage. In some applications the alternating current to be rectified is at a much lower voltage; an example of this is an industrial current at 110 or 220 volts. In these cases, again, it is desired to obtain rectified currents exceeding an ampere and even, if possible, ten amperes. One of the occasions when the problem takes this form is that of charging accumulators in localities where the electric supply is alternating.

It is possible, however, to construct thermionic rectifiers satisfying these new conditions, but it becomes necessary to introduce into the tube a gas of a suitable nature and pressure. The discharge then partakes more or less of the characteristics of an arc; ionization by collision is made use of, resulting in a greatly increased current yield. On the other hand, the voltage across the terminals of the tube is considerably decreased and, as with ordinary arcs, may fall to a few volts.

A large number of types of apparatus have been proposed in this connexion. As they do not differ essentially from ordinary arc rectifiers, for example, from mercury arc

rectifiers,* we shall not devote very much time to them. It will be sufficient to describe one type made in America, where it has spread with extraordinary rapidity, and where it is commonly used nowadays for charging accumulators. This is the ' Tungar ' lamp,† which owes its name to the facts that its incandescent cathode is made of tungsten and that the gas used is argon. One model of the Tungar lamp is shown in Fig. 24. The filament of this lamp is a

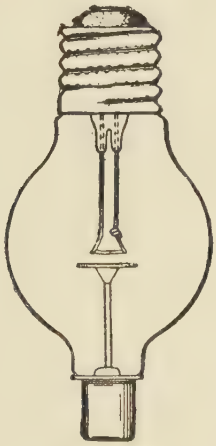

FIG. 24

tungsten wire heated by an independent battery of accumulators, or better still by the alternating current to be rectified. To this end a small step down transformer is connected to the alternating supply and its secondary put across the filament. The anode is of tungsten, graphite, or other refractory material, according to the circumstances. The gas contained in the tube is argon, at a pressure when cold of between 3 and 8 cm. of mercury. Experience has

* See M. Leblanc fils, *L'Arc Électrique.*

† G. S. Meikle, *General Electric Review*, 1916, 19, 297.

shown that under these conditions the disintegration of the filament by the bombardment of the positive ions is reduced to a minimum, whilst the thermionic emissive power of the tungsten is integrally conserved. The latter result only holds if perfectly pure argon be used, and if its purity be maintained with the lapse of time. For this purpose a purifying substance is introduced into the tube in order to absorb traces of active gases (oxygen, etc.) which may be liberated and to prevent them from reacting chemically with the filament. In the tungar lamps at present in commercial use the purifying substance is often a deposit of metallic calcium covering all the interior walls of the tube.

The two smallest types of tungar are capable of rectifying up to two amperes and up to six amperes respectively. Some models have been constructed which are capable of rectifying several tens of amperes. A third auxiliary electrode is then necessary in order to start the discharge ; this is usually a small incandescent tungsten wire. In the small models, on the other hand, it is often possible, after the arc has been started and the rectifier is working regularly, to switch off the filament heating current and consequently to eliminate the loss of power which this involves ; in fact, the arc itself liberates sufficient heat to maintain the filament at incandescence. There is only a tendency for it to concentrate on a very narrow region of the cathode, and this is not favourable to the life of the lamp. Normally these tubes have a life which attains and exceeds 1,000 hours.

CONCLUSION

THE foregoing account enables us to review the correctness of the statements which were made at the commencement. The study of thermionic phenomena, in spite of the remarkable theoretical and experimental progress which has taken place during the last few years, is still developing rapidly. The practical advances have been particularly remarkable, and they have already resulted in the birth and development of some important industries. Hundreds of thousands of two and three electrode tubes have been manufactured for the needs of radiography, of wireless telegraphy, of alternating current rectification, and so on. But in spite of these technical advances, which have been rendered possible by the progress of purely scientific investigation, the work of the latter is far from being accomplished. There is still only very insufficient information concerning the relations which are known to exist between thermionic phenomena and other phenomena known for a longer time, such as contact potential differences, thermoelectric phenomena, and so on. The study of thermionic emission in gaseous media has also encountered very great difficulties and it is for the future to remove all the experimental contradictions which exist in this domain. Many substances have not yet been examined from the thermionic point of view, or have received insufficient attention. The study of ionization and resonance potentials based on the employment of the thermionic emissions has scarcely commenced. In short, as time goes on this domain should appear more complex, but also richer in theoretical and experimental suggestions. Moreover, it is to be expected that these questions will be found to continue both to develop rapidly and to serve as material for the researches of physicists.

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